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THE CHEMISTRY OF WATER AND SEWAGE TREATMENT

BY
ARTHUR M. BUSWELL 1888–
CHIEF, ILLINOIS STATE WATER SURVEY. PROFESSOR OF SANITARY CHEMISTRY, UNIVERSITY OF ILLINOIS.

American Chemical Society
Monograph Series

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

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Preface

This monograph, as its title implies, is intended to present as completely as possible the information available concerning the chemical reactions taking place in the various processes by means of which water is improved for domestic and industrial use and waste liquors are rendered fit to be discharged into water courses. A general knowledge of the mechanical steps involved and the general layout of various types of treatment plants is essential to a coherent understanding of the chemical operations. This phase of the subject has been covered by means of pictures, diagrams and description. But we have consciously avoided a detailed discussion of the construction and operation of mechanical devices. The subject of analytical methods has also been omitted. Both these topics have been admirably treated by other writers. We are not aware of any previous work dealing solely with the chemistry of the various purification processes at present applied to water and sewage.

It has been the aim of the author to cover the literature as thoroughly as possible down to the date of publication. A bibliography of over four thousand references has been compiled during the preparation of this work.

The writer is more and more impressed with the fact that these treatment methods are just as truly chemical manufacturing processes as are the production of sugar and dyes. The raw materials which must be refined are unique in that they contain very minute amounts of exceedingly objectionable substances. One ten-thousandth of one per cent of iron in a water supply will cause thousands of dollars' worth of damage annually. Relatively strong sewage contains but a few hundredths of one per cent of organic matter. Not only are the impurities minute in amount but they are exceedingly variable in their occurrence. It is not unusual for the chemical composition of a water to vary several per cent in the course of a few hours. City wastes vary from a high organic content to almost zero from noon to midnight every day and there are also weekly variations and variations in quality with the seasons. The variation in the quantity of material that must be handled is almost as great as the variation in quality. Another cause

of difficulty in these purification processes is the lack of a common yard stick. While testing methods are constantly being improved we are far from being able to assay a water or a waste as we might assay an ore. Lacking a common denominator it is difficult from the success of a certain modification or improvement in one installation to draw conclusions as to the probable success of the improved process elsewhere. Each water supply, each waste liquor and each swimming pool has its individual problem which must be considered before successful treatment can be expected.

The field of water and waste treatment is probably farther from the "saturation point" which sales managers worry about than most chemical industries. While the majority of the urban population is served with a disinfected potable water, a comparatively small percentage is supplied with a palatable water. The treatment of industrial supplies, although known and practiced for nearly a hundred years, is still in its infancy. Waste treatment is perhaps the most backward. Only a few of our larger cities treat their wastes adequately, while industrial wastes are in most cases discharged untreated.

The many recent applications of physical chemistry to this field made it seem advisable to present a brief review of those subjects for the benefit of the chemist who had gotten away from chemical theories and the engineer who may have never had occasion to study them. In the preparation of the chapters on chemical theory (I and II) the author has made extensive use of various standard texts, more especially Stieglitz's *Qualitative Analysis,* Washburn's *Physical Chemistry* and Lewis' *Valence.* He is greatly indebted to Prof. W. H. Rodebush and Dr. T. E. Phipps of the University of Illinois for helpful suggestions on Chapter I. Prof. A. W. Thomas of Columbia University (N. Y.) made a great many valuable suggestions with regard to the matter in Chapter II. Mr. J. W. Elms and Mr. G. C. Habermeyer have suggested several simplifications in Chapters I and II. Mr. S. L. Neave and Mr. A. L. Elder have been of invaluable assistance in the correction of manuscript and proof. The careful work of the editors and publishers has resulted in much improvement over the original manuscript in composition and diction. Their labors are gratefully acknowledged. The author wishes to express his thanks to the many other friends and associates who have offered valuable criticisms and suggestions.

The sources of illustrations, diagrams and citations are indicated by references in the text.

Urbana, Illinois, August, 1927.

A. M. Buswell.

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THE CHEMISTRY OF WATER AND SEWAGE TREATMENT

Chapter I.

Notes on Chemical Theory.

Structure of Atoms and Theory of Valence.

The theory of chemical valence—the forces or conditions which hold atoms together in molecules and determine what molecules will be formed and whether or not they will be stable—is probably the most fundamental conception in chemistry. In a merely qualitative way it is referred to as "chemical affinity." Our understanding of this theory will determine our ability to predict what chemical changes will take place and to what extent, whether a given liquor will corrode a certain alloy, what reagent will remove a given type of turbidity or color, and what are the best conditions for filter-pressing sewage sludge.

Some very important and helpful advances have been made recently in our knowledge of valence and chemical affinity which, though quite generally accepted as fundamentally correct, have not been known long enough nor been sufficiently elaborated to be included in elementary texts. So for the benefit of the engineer and the technical chemist who may not have found opportunity to follow the subject we shall present a brief summary of atomic structure and valence as they are now regarded by physicists and physical chemists. A more complete popular discussion may be found in Lewis' Monograph—*Valence and the Structure of Atoms and Molecules.*

The idea that the atoms of the different elements were composed of some simple substance or substances is by no means new. The early alchemists believed, or, perhaps better, hoped that this was so, as their attempts to transmute the baser elements into gold testify. The relation between the atomic weights and chemical properties, developed into the periodic arrangements of the elements by Mendelejeff, was perhaps the first real evidence or indication of the common origin of the elements.

Conclusive proof is furnished by the study of radioactive elements which are continually decomposing to yield elements of lower atomic weight. For example, uranium breaks down forming radium and eventually helium, and radium continues to break down forming helium and lead as end products. This observable "transmutation" of the radioactive elements together with other evidence has led to the modern theory of the structure of chemical atoms based on the assumption that the atoms of all elements are composed of the same material.

This basic material of which the elements are supposed to be composed is made up of positive and negative charges of electricity. Thus the only difference between gold and oxygen is in the number and arrangement of these electrical charges within the respective atoms.

Atoms of the elements are believed to be like miniature solar systems with a small, very compact, positively charged body, the nucleus, at the center, surrounded by electrons, the number of these electrons corresponding to the positive charge on the nucleus.

The electron is a small negatively charged particle, the "atom" of negative electricity. All electrons are equally charged and the value of this charge is the unit in terms of which nuclear and ionic charges are expressed. A group containing a nucleus with 8 positive charges and 8 electrons will be electrically neutral; if it contains 9 electrons it will have 1 negative charge; and if it has only 7 electrons it will have a net of 1 positive charge, etc.

As a result of investigations of the X-ray spectra of the elements and other data, discussion of which we cannot include here, the elements have been arranged in a series beginning with hydrogen as one. The series is given in Table 1.

The serial number of each element, called its "atomic number," corresponds to the number of unit positive charges on the nucleus and also to the number of planetary electrons. This atomic number we shall find is very useful in classifying chemical properties.

It has been possible to estimate the size of the nucleus and it appears to be about 1×10^{-12} to 1×10^{-13} cm. in diameter or about one-ten thousandth of the diameter of the average molecule. The electron is apparently much more bulky but its mass is only about one-two thousandth of that of the hydrogen nucleus. The mass of the atoms is therefore in the nucleus, the electron weights being negligible.

The hydrogen atom is, of course, the smallest and simplest. It consists of a nucleus with one positive charge and one electron. The system is thus electrically neutral. The next larger atom, helium (atomic number 2), has a nucleus with two positive charges and two electrons.

The two electrons of helium are apparently arranged symmetrically about the nucleus thus · ● ·. This group is apparently very stable and throughout the series of chemical elements we always find a pair

TABLE 1.—*Atomic Numbers of the Elements.*

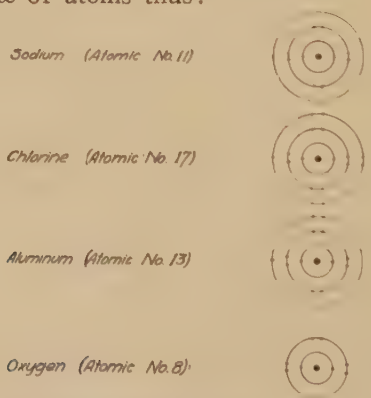
Hydrogen	1	Silver	47
Helium	2	Cadmium	48
Lithium	3	Indium	49
Beryllium	4	Tin	50
Boron	5	Antimony	51
Carbon	6	Tellurium	52
Nitrogen	7	Iodine	53
Oxygen	8	Xenon	54
Fluorine	9	Cesium	55
Neon	10	Barium	56
Sodium	11	Lanthanum	57
Magnesium	12	Cerium	58
Aluminum	13	Praseodymium	59
Silicon	14	Neodymium	60
Phosphorus	15	Illinium	61
Sulfur	16	Samarium	62
Chlorine	17	Europium	63
Argon	18	Gadolinium	64
Potassium	19	Terbium	65
Calcium	20	Dysprosium	66
Scandium	21	Holmium	67
Titanium	22	Erbium	68
Vanadium	23	Thulium	69
Chromium	24	Ytterbium	70
Manganese	25	Lutecium	71
Iron	26	.....	72
Cobalt	27	Tantalum	73
Nickel	28	Tungsten	74
Copper	29	.....	75
Zinc	30	Osmium	76
Gallium	31	Iridium	77
Germanium	32	Platinum	78
Arsenic	33	Gold	79
Selenium	34	Mercury	80
Bromine	35	Thalium	81
Krypton	36	Lead	82
Rubidium	37	Bismuth	83
Strontium	38	Polonium	84
Yttrium	39	.....	85
Zirconium	40	Niton	86
Columbium	41	.....	87
Molybdenum	42	Radium	88
.....	43	.....	89
Ruthenium	44	Thorium	90
Rhodium	45	.....	91
Palladium	46	Uranium	92

of electrons near the nucleus as in the case of helium, while the additional electrons assume more distant positions. The number of electrons increases with the atomic number or charge of the atomic nucleus. This raises the question of the arrangement of the electrons about the

nucleus. As the number increases to ten there is a tendency for the last eight to arrange themselves in pairs at the points of a tetrahedron, e.g., in oxygen with eight electrons we have the arrangement with the fourth point of the tetrahedron vacant. Neon, a rare and inert gas with ten electrons about its nucleus would have a pair at each of the four apices. As the size of the atoms increases there is a tendency for the additional electrons to form another tetrahedron.

As we continue up the list to elements whose atoms contain nuclei with thirty or more positive charges and a corresponding number of electrons the arrangement of electrons becomes more complicated. It is convenient to consider them as lying at the surfaces of concentric spheres or shells having the nucleus as a common center. The first shell can apparently contain two electrons and no more, the next shell can hold eight but no more. From considerations to be mentioned later it appears that the third shell may be completed by either eight or eighteen electrons.

The electrons are undoubtedly revolving in orbits about the nucleus as the earth revolves about the sun, and the centers of these orbits appear to occupy certain fixed positions. In representing atomic structure in figures where dots are used to indicate nuclei and electrons, or in referring to positions of electrons, it will be understood that the positions of the centers of their orbits are meant. In order to avoid the difficulty of drawing solid figures the electrons will be shown as lying in circles instead of at the surfaces of spheres. We may then indicate the formulæ of atoms thus:



These formulæ may be abbreviated by using the usual chemical symbol to indicate the nucleus and all but the last shell of electrons, e.g.,

Relation of Structure to Chemical Properties.

In the previous paragraphs we intimated that the electron shells about the atomic nucleus seemed to have a capacity for a definite number of electrons and that after the first shell of two, there is a tendency to form octets or groups of eight electrons. Whatever may be the physical reason for this tendency for octet arrangement the fact is of great importance in interpreting and predicting chemical properties. For example, atoms with completed shells are very inert and unreactive, in fact, they seldom if ever form chemical compounds or enter into chemical reactions. The inert or "noble" gases, helium, neon, argon, etc., have such structures. On the other hand, atoms whose outer shells are not geometrically complete are reactive chemically, e.g., sodium with eleven electrons, arranged 2—8—1, is, of course, an active chemical element, while neon with ten electrons arranged 2—8 is entirely inert. Chlorine with a nuclear charge of + 17 and 17 electrons arranged in 3 shells (2—8—7) is very reactive, while argon with a nuclear charge of 18 and 18 electrons arranged 2—8—8 is inert. It appears therefore that shells of electrons containing 2 or 8 electrons (in the lighter elements) are exceedingly stable, this stability being due to the geometrical symmetry of electron arrangement rather than to electrical or magnetic forces. Atoms which are electrically neutral but with incomplete shells show a tendency to share electrons with other atoms or even take electrons from or give electrons to other atoms in order that complete shells may be formed, although in so doing they may become positively or negatively charged due to the loss or gain of electrons. In this tendency of atoms to arrange themselves so that their electron shells may take on as nearly as possible the stable configuration of the octet we seem at present to see the cause of chemical properties and reactions. Another important observation which has been very useful in explaining chemical reactions is that of G. N. Lewis [1] who points out that there is a marked tendency for electrons to become associated in pairs. If eight electrons were equally spaced in a shell they would form the corners of a cube but being associated in pairs they correspond to the corners of an inscribed tetrahedron.

[1] American Chemical Society Monograph—*Valence and the Structure of Atoms and Molecules.*

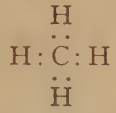
Theory of Valence.

In the preceding discussion of stable configuration we have referred to the sharing and transfer of electrons in order to form complete or stable shells. The inner shells of electrons are complete and stable and must be distinguished from the outermost shells. We shall do this by referring to the latter as "valence electrons" since they appear to be responsible for the formation of chemical compounds.

When we compare the number of electrons in the outer shells of the various elements, the "valence electrons," with the numerical valences according to the older views, there appear at first to be serious discrepancies. Oxygen, for example, has six valence electrons, chlorine seven and nitrogen five. Hydrogen, however, has one valence electron, sodium one, magnesium two, aluminum three and calcium two. Since in some cases the number of valence electrons corresponds to the "valence" in its older sense and in some cases it does not, we must conclude that the two are not identical. As we follow the formation of molecules by atoms we shall see that the main trouble with the old notion of valence is that it tells only part of the story.

A few examples of molecular structure will help to illustrate how these valence electrons function. Let us take first the compound in which we are most interested, water, H_2O. This compound is made up of two hydrogen atoms each with one valence electron and one oxygen atom with six valence electrons. The system then contains the necessary eight electrons to form the stable octet about the oxygen which we can represent on a plane surface thus: $:\dot{\underset{\cdot\cdot}{O}}:$ This arrangement would have two negative charges due to the addition of two electrons to the oxygen atom and would be the "oxide" ion, and the hydrogens, robbed of their electrons, would be hydrogen ions (H^+). But there is a further possibility for the formation of a stable geometrical figure, namely, the association of each hydrogen nucleus with a pair of the electrons of the octet, which as mentioned above gives the very stable geometrical form of helium. Two pairs of electrons then serve both to complete the oxygen octet and to form the doublets for the hydrogen. They appear to be "shared" by the oxygen and the hydrogen, and we have a molecule which is electrically neutral and geometrically stable and which may be represented thus: $H:\dot{\underset{\cdot\cdot}{O}}:H$. These pairs of shared electrons correspond to the "bond" or "valence" in its former sense. Similarly methane, "marsh gas," (CH_4) is formed when a carbon atom

with four valence electrons shares them with four hydrogen atoms, completing its own octet and providing each hydrogen atom with a doublet thus:

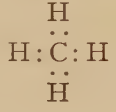


In one case, water (H_2O), two pairs of electrons are shared by oxygen and hydrogen and in the other, methane (CH_4), four pairs are shared by the carbon and hydrogen atoms. In both cases the hydrogen is firmly bound, more firmly in methane than in water as will be explained later.

On the other hand, if hydrogen and chlorine combine, the hydrogen having one valence electron and the chlorine seven, an octet is formed but the chlorine appears to take nearly complete possession of the "shared" pair of electrons, thus practically gaining one electron and becoming negatively charged, while the hydrogen atom having lost an electron is positively charged. The electrical attraction between the oppositely charged atoms together with the unequally shared pair of electrons is the primary force which is sufficient to hold them together except when dissolved in a liquid of high dielectric constant like water. When dissolved in water hydrogen with a positive charge and no electron (hydrogen ion) and chlorine with a negative charge and a complete octet (chloride ion) separate or ionize (*see* p. 24). Similarly when sodium which has one valence electron combines with chlorine to form sodium chloride the chlorine again takes complete possession of the bonding pair of electrons and an ionizing compound is formed (p. 27). By this transfer of an electron both sodium and chlorine conform to the rule of eight. The electron from the sodium completes the chlorine octet and the sodium after losing an electron is left with an octet as its outer shell.

The difference in the properties of compounds which show electrical polarity, that is, positive and negative groups in the molecule like sodium chloride, and the non-polar compounds like methane required two explanations of valence according to the older theory. The polar compounds (the electrolytes—acids, bases and salts) were considered as being held together by electrical forces acting between positively and negatively charged atoms or groups of atoms, while the non-polar class of compounds, composed largely of carbon or "organic" compounds, were supposed to be held together by "bonds." The difficulty with two explanations for valence or "chemical affinity" is that

the two classes of substances, polar and non-polar, to which they apply respectively, are not sharply separated nor well defined. We find all gradations between the highly polar sodium chloride and the non-polar methane. This indicates a difference in degree rather than in kind. The newer theory of valence gives us one and the same cause for the formation of sodium chloride and methane, namely, the tendency to complete the octet and the tendency of electrons to form in pairs. The shared pairs of electrons are the "bonds" of organic chemistry and at the same time the relative position of these shared pairs of valence electrons between the combining atoms determines whether a polar or non-polar compound will be formed. In methane



for example, the bonding pairs may be considered as equidistant between the hydrogen and carbon nuclei; in water H:Ö:H the bonding pairs are drawn in slightly to the oxygen nucleus and the compound is very slightly polar forming a very small amount of hydrogen ion (H^+) and hydroxyl ion (OH^-), while in sodium chloride (Na :Cl) the bonding pair is so strongly drawn into the chlorine shell that when sodium chloride is dissolved in water it dissociates almost completely into Na^+ and Cl^-.

In general we may observe that those atoms which have less than three valence electrons are relatively strong bases, while those with more than five are strongly acid. Sodium (one valence electron) and calcium and magnesium (two valence electrons each) are strong bases while aluminum (three valence electrons) is weakly basic and under some conditions, weakly acid. Sulfur with six valence electrons and chlorine with seven are acid.

Here we have a very simple explanation of the difference between basic and acid, or as they are sometimes called, positive and negative elements. An acid or negative element is one which tends to draw toward itself the electrons in the outer shells of all neighboring atoms and a positive or basic element is one which attracts these electrons to a less extent. Between these two we have the elements which tend to form non-polar compounds like the hydrocarbons.

The usefulness of this theory is further shown by the fact that we do not have to make special cases to fit inorganic and organic compounds, and a remarkable confirmation of its correctness is the

fact that out of some hundreds of thousands of known chemical substances all but a very few conform to the octet and doublet rules and these few show unusual properties which would be predicted by their irregular structures.

Law of Mass Action and Reversibility of Chemical Reactions.

The notion that the course of chemical reactions is affected by the "active mass" of the reacting substance was suggested very early in the history of the science. It was in 1799 that Bertholet pointed out that certain Egyptian deposits of sodium carbonate were the result of action of high concentrations of salt which caused the reversal of the ordinary reaction: $CaCl_2 + Na_2CO_3 \rightleftarrows CaCO_3 + 2NaCl$.

He suggested that a large quantity of material might overcome a weak "affinity." Subsequent workers added evidence of the correctness of this assumption and in 1867 Guldberg and Waage formulated what we now call the law of mass action. This law states that the rate at which a substance reacts is proportional to its "active mass" and that the velocity of a chemical reaction is proportional to the active masses of the reacting substances. It further implies that all reactions are reversible. To restate this law by means of equations, let us consider the case of two substances **A** and **B** which react to form two other substances **C** and **D** thus:

$$\mathbf{A} + \mathbf{B} \rightleftarrows \mathbf{C} + \mathbf{D}. \tag{1}$$

The velocity to the right (V_1) is proportional to the products of the active masses (in general the concentrations) of **A** and **B** which we will indicate thus $[A]$ and $[B]$. If we let K be the proportionality constant we may write

$$V_1 = K_1 \times [\mathrm{A}] \times [\mathrm{B}]. \tag{2}$$

Likewise for the velocity to the left (V_2) we may write

$$V_2 = K_2 \times [\mathrm{C}] \times [\mathrm{D}]. \tag{3}$$

At equilibrium **C** and **D** react to form **A** and **B** at the same rate that **A** and **B** react to form **C** and **D** so that $V_1 = V_2$. Therefore for equilibrium conditions we may combine (2) and (3):

$$K_1 \times [\mathrm{A}] \times [\mathrm{B}] = K_2 \times [\mathrm{C}] \times [\mathrm{D}]$$

or

$$\frac{K_1}{K_2} = K = \frac{[\mathrm{C}] \times [\mathrm{D}]}{[\mathrm{A}] \times [\mathrm{B}]} \tag{4}$$

Equilibrium is seen in this formula as a dynamic, not as a static con-

dition. Chemical reaction is not at a standstill but is proceeding with equal velocity in opposite directions. The equilibrium constant K expresses the ratio of the two velocity proportionality constants K_1 and K_2.

This law may be derived mathematically in several ways. Perhaps the simplest is based on the kinetic theory. In the reaction given above (1) we consider that the molecules of the substances **A** and **B** are in rapid random motion. The rate at which **A** and **B** react to form **C** and **D** will depend on the number of collisions of **A** molecules with **B** molecules per unit of time, and the number of collisions will in turn be proportional to the number of **A** molecules and **B** molecules in a unit volume. The number per unit volume is the concentration or active mass referred to above so we may write

$$V = K \times [\mathrm{A}] \times [\mathrm{B}]$$

which is identical with equation (2). Equation (3) follows by the same method of reasoning and equation (4) or the mass law follows from (2) and (3).

The usefulness of this law is apparent when we consider that it indicates a method for controlling the results of chemical reaction. If, for example, in equation (1) we wish to increase the amount of C at equilibrium we may do so first by increasing the amount of A, second by increasing the amount of B, or third by decreasing the amount of D. Any one of these changes will necessitate the increase of C in order to satisfy the law as formulated in equation (4).

As stated above the law of mass action apparently covers all chemical reactions. In practical application difficulty is sometimes encountered in properly determining the "active mass" or the "activity" or as it has sometimes been called "effective concentration" value for the reacting substances. This difficulty will not lessen its usefulness for the purposes of the present discussion.

The field in which the law of mass action has perhaps found its greatest usefulness is that of chemical reactions in solutions. It is for the purpose of applying it to such reactions that it has been developed here. Since most of the substances to be dealt with are ionized in water solution, a summary of the more important points of the ionization theory will be necessary before making this application.

Ionization.

Evidence of Ionization.

Certain characteristic properties of solutions are attributed, by the kinetic theory, to the number of particles (molecules) of the dissolved

substance present in a unit volume of the solution. One such property is osmotic pressure. If we close the large end of a thistle tube with a collodion membrane, fill it partially with any solution and invert it in a beaker of distilled water as shown in Figure 1 we find that water will pass through the membrane into the tube causing the level

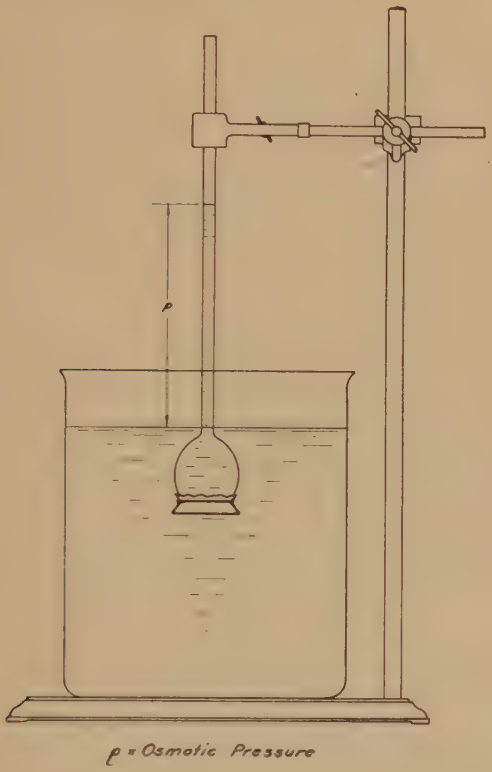


FIG. 1.—Osmotic Pressure (after Bary).

to rise. That the osmotic pressure which causes this rise in water level in the tube is dependent upon the number of molecules per unit volume, i.e., the molecular concentration of the solution, is demonstrated by the fact that equal osmotic pressures are shown not by solutions of equal concentration by weight but by those of *equivalent molecular* concentration. For example, 342 gm., or a gram-molecular weight, of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 cc. of water exhibits the same osmotic pressure as 180 gm. of glucose ($C_6H_{12}O_6$) or 90 gm. of glycerin ($C_3H_8O_3$) shows when dissolved in a similar amount of water.

Another characteristic effect of dissolved substances is the raising of the boiling point and the lowering of the freezing point of the solvent. If we were to determine the boiling points and freezing points of the three solutions just mentioned we would find them all affected to the same degree. They boil at approximately 100.52° C. and freeze at — 1.89° C. The concentration in grams varies widely but the number of molecules is the same per unit volume. The number of solutions which have been found to give an osmotic pressure and an increase in boiling point and a decrease in freezing point proportional to their gram molecular or "molal" concentration is sufficiently large to justify referring to these effects as "normal."

There is, however, a large group of common substances which when dissolved in water show abnormal osmotic pressures and abnormal boiling point and freezing point effects. A solution of sodium chloride containing 58.45 gm. per 1000 cc. of water, i.e., a "gram molecular" or "molar" solution, boils at 100.94° C. and freezes at — 3.42° C. This effect is nearly twice as great as that produced by the sugars, etc. The osmotic pressure effect of the sodium chloride solution is correspondingly abnormal. Abnormal effects, though varying somewhat in degree, are shown by water solutions of all acids, bases and salts. Our only conclusion is that when these substances are dissolved in water a larger number of particles are present than would be expected. This must mean that some of the molecules themselves are broken up in solution to form smaller particles. These "sub-molecules" are called "ions" and the process by which they are formed is ionization.

Electrical Conductivity of Solutions.

Another important point for consideration is the electrical conductivity of these two types of solutions. The solutions of such substances as sugar, glycerine, alcohol, etc., are practically non-conductors while solutions of acids, bases, and salts are good conductors. In fact, the substances in the latter group which are the best conductors such as hydrochloric acid, sodium hydroxide, sodium chloride, etc., also produce the greatest abnormal effects on the boiling point, freezing point and osmotic pressure. Apparently, then, conductivity in solution depends upon the ions, and the degree of ionization is proportional to the conductivity. Experimental data indicate that this is quantitatively true.

If the ions carry the current they must be electrically charged and the sign of the charge may be determined by finding the direction

which they take in so doing. Thus for sodium chloride we know from experiment that the sodium is positive and the chlorine is negative, so we may write

$$NaCl \rightleftarrows Na^{+} + Cl^{-}.$$

Ionization, it should be remembered, is not dependent upon an electric current. The ions are already formed in the solution. The difference of potential, if applied, merely causes them to travel toward the respective poles.

It will be noted that this discussion has been limited to water solutions. The abnormal effects referred to are observed to a lesser extent in alcoholic solutions and still less or not at all in most other solvents. Hydrogen chloride dissolved in benzene is a non-conductor and gives normal boiling point and freezing point effects.

Ionization and Reactions.

Ionized substances react differently from un-ionized substances. The ionic theory would not be of much value to the chemist if this were not so. As an example, hydrogen chloride in water we know attacks marble ($CaCO_3$) with the rapid evolution of carbon dioxide but if a chunk of marble is dropped into a solution of hydrogen chloride in dry benzene there is no reaction. Since hydrogen chloride is ionized in water but not in benzene it is apparent that the reaction is due to the ionized rather than the un-ionized acid.

In subsequent chapters numerous examples will be met with which show that reactions in water solutions take place between ions and are practically independent of the presence of un-ionized molecules.

Cause of Ionization.

In considering the facts just described two questions arise. The first is, why do certain substances ionize while others do not; and the second is, why do ionizing substances show this property when dissolved in water but not in such solvents as benzene.

The answer to the first question has been given in part in the discussion of polar and non-polar compounds (p. 21). Here it was pointed out that electro-negative elements like chlorine tend to draw in the bonding pairs of electrons and become negatively charged while basic or electro-positive elements like sodium or potassium are not able to hold the bonding pair against the attraction of the electro-negative element. Thus the bonding pair is displaced toward the acid element and a polar compound results. Such compounds with

the bonding pair displaced dissociate to form ions when dissolved in solvents having high dielectric constants. Non-polar compounds like the sugars or mineral oils, etc., in which the bonding pairs are not displaced do not dissociate.

The effect of the solvent on ionization is apparently due to its ability to neutralize the electrical attraction between the positive and negative ions. The degree to which a given salt is ionized in various solvents is proportional to the dielectric constants of those solvents. This is shown on page 65. Since water has a very high dielectric constant it is effective as an ionizing solvent. It has also been observed that the molecules of ionizing solvents tend to associate into groups of two or three when in the liquid state. Liquid water, for example, is composed largely of $(H_2O)_2$. Non-ionizing solvents do not show this property.

Strong and Weak Electrolytes.

There is no sharp line of demarkation between substances that ionize and those that do not. We find substances like sodium chloride which is nearly completely ionized in water; substances like acetic acid which is only two percent ionized; and still further substances like water itself or hydrogen sulfide which give only a minute trace of ions. The formulæ for acetic and nitric acids may be written showing only the hydrogen-oxygen bonding pairs of electrons, thus:

$$H : OCOCH_3 \text{ and } H : ONO_2.$$

Carbon is neither positive nor negative but oxygen is slightly negative so the effect of the group OCO is to pull in slightly the pair of electrons which holds the hydrogen and the result is a weak or slightly ionizing monobasic acid. Nitrogen on the other hand is more electronegative than carbon and with the three O atoms forms a group which pulls in the bonding pair very strongly so that nitric acid is highly ionizing.

Carbonic and sulfuric acids furnish another useful comparison. The partial structural formulæ would be

$$\begin{matrix} H : O \\ \quad CO \\ H : O \end{matrix} \qquad \text{and} \qquad \begin{matrix} H : O \\ \quad SO_2. \\ H : O \end{matrix}$$

In carbonic acid we have the "neutral" carbon atom and three oxygens exerting a pull on the two electron pairs which hold the two hydrogens. This results in a very slight displacement and, as we know, carbonic acid is very weak, i.e., slightly ionized. Sulfur, however, is

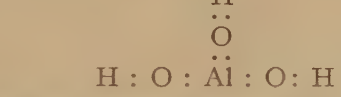
a distinctly electro-negative element [2] and with the four oxygens forms a group which draws the hydrogen binding electrons in strongly, so that sulfuric acid is a strong or highly ionizing acid.

A similar explanation may be given for the existence of strong and weak bases and highly ionizing and weakly ionizing salts.

In the case of the bases we have the typical formula M : OH, where M stands for an electro-positive element. These elements repel the bonding pair which they share with oxygen and hence ionize thus: M^+ $^-$: OH.

Amphoteric Compounds.

As mentioned on page 22 some elements may be either weakly electro-negative (acid) or electro-positive (basic). They are called amphoteric. Aluminum hydroxide is an important example. The formula may be written



Here the hydrogen-oxygen bonding pairs on both sides of the oxygens appear to be displaced but only slightly so that under some conditions the compound acts as a base, forming aluminum ions (Al^{+++}) and hydroxyl ions (OH^-), and under other conditions it acts like an acid, forming aluminate ions (AlO_3^-) and hydrogen ions (H^+). The properties of aluminum will be discussed more fully under *Water Purification* (p. 165).

Application of Law of Mass Action to Ionization.

The application of the law of mass action to the reaction of ionization has been very extensively investigated. The law has been found to hold with quantitative accuracy for dilute solutions of the less highly ionized acids, bases and salts but data obtained with strong electrolytes are not so easily reconciled with its predictions. It is probable that in the latter case the apparent discrepancies arise from an inability to determine all of the factors affecting the experimental data rather than in any fundamental error in the law. Since a large number of the reactions to be met with in the present discussion conform

[2] The inconsistency of calling negative, an element which like chlorine has so strong an attraction for the negative electron results from our inability to discard our older terminology all at once. The change has already been suggested and it is probable that eventually metals will be referred to as negative and acids as positive elements.

to the law of mass action without special modification and since even in its elementary form the law applies qualitatively to reactions in solutions in general we shall avoid the lengthy discussion which a complete presentation would require.

Ionization Constant.

The equation for the ionization of a simple acid like acetic whose formula for convenience we shall write HAc may be written

$$HAc \rightleftarrows H^+ + Ac^- \qquad (5)$$

Adopting the convention that a formula in brackets thus [HAc] indicates the concentration of the substances in multiples or fractions of the gram formula weight per liter we may substitute the members of equation **(5)** in the mass law thus

$$\frac{[H^+] \times [Ac^-]}{[HAc]} = K. \qquad (6)$$

This K is known as the ionization constant of acetic acid. It may be determined by a number of physico-chemical methods (boiling point, conductivity, etc.,) and once accurately known serves to define solutions of acetic acid.

As previously pointed out (p. 23), the amount of one substance in a reversible reaction may be changed by altering the amount of one or more of the other reacting substances. If, for example, we have a solution of acetic acid with too high a hydrogen-ion concentration, this may be remedied by adding sodium acetate. Sodium acetate is highly ionized ($NaAc \rightleftarrows Na^+ + Ac^-$) and greatly increases the acetate-ion concentration. This increases the value of the numerator in equation **(6)**; equilibrium is disturbed and can only be re-established by the reversal of reaction **(5)**. Some H^+ combines with Ac^- to form HAc and the result is a decrease in the hydrogen-ion concentration. This is known as the "common ion effect" and is one of three means of controlling ionic reactions.

A second way to alter the concentration of a given ion is by adding an ion with which it will combine to form a very slightly ionized compound. Carbonic acid ionizes *very* slightly according to the equation

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

Or in other words K of the formula

$$\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = K \qquad (7)$$

is very much smaller than K for acetic acid (equation 6). If we add to our HAc solution sodium bicarbonate ($NaHCO_3$) which ionizes, thus:

$$NaHCO_3 \rightleftarrows Na^+ + HCO_3^- \tag{}$$

there will be much larger amounts of hydrogen ion and bicarbonate ion than are consistent with equation (7). As a result carbonic acid, H_2CO_3, will have to be formed and some hydrogen ion will be used up. Thus in a second way we have decreased the hydrogen-ion concentration. It is true that this reaction causes a disturbance of the equilibrium of reaction (5) causing some HAc to ionize forming hydrogen ion and acetate ion. But sodium acetate is almost completely ionized so that very few acetate ions are used up. The net effect is therefore a substantial decrease in hydrogen-ion concentration. These reactions are best represented as follows:

$$\begin{array}{ccccc} HAc & \rightleftarrows & H^+ & + & Ac^- \\ & & + & & + \\ NaHCO_3 & \rightleftarrows & HCO_3^- & + & Na^+ \\ & & \downarrow\ \uparrow & & \uparrow\downarrow \\ & & H_2CO_3 & & NaAc \end{array} \tag{8}$$

The weight of the arrows represents approximately the relative numerical values of the ionization constants.

A third method of decreasing the hydrogen-ion concentration is by the formation of an insoluble product. Carbonic acid as is well known is only slightly soluble. When a certain concentration is reached it decomposes giving off gaseous carbon dioxide:

$$H_2CO_3 \rightleftarrows H_2O + CO_2. \tag{9}$$

If, after adding sodium bicarbonate as above till the solution is saturated with H_2CO_3, the hydrogen-ion concentration is still too high, it may be further decreased by adding still more bicarbonate. As long as the product $\dfrac{[H^+] \times [HCO_3^-]}{[H_2CO_3]}$ exceeds the value K in (7) carbonic acid will have to be decomposed according to (9) in order to re-establish equilibrium. This reaction uses up hydrogen ion and its concentration is decreased. A similar result could be obtained by the addition of a salt of silicic acid. In this case an insoluble precipitate of silicic acid would be formed. Hydrogen ion would be used up as before and the hydrogen-ion concentration decreased.

To summarize: the application of the mass law to ionization indicates three ways in which the concentration of a given ion may be decreased: (1) by adding a salt containing the ion with which it was

combined before ionization (the "common ion" effect); (2) by adding a salt containing an ion with which it forms a very slightly ionized compound; and (3) by adding a compound containing an ion with which it forms an insoluble compound (either gas or solid).

The Ion-Product Constant of Water.

A very useful relation between acids and bases is brought out by applying the mass law to the ionization of water. Water as previously mentioned ionizes to a slight extent according to the equation:

$$H_2O \rightleftarrows H^+ + OH^- \qquad (10)$$

and according to the mass law

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = K. \qquad (11)$$

But the amount of water present is so enormous in proportion to the amount of its ions that its concentration in mols per liter ($^{1000}/_{18}$) for all practical purposes remains constant. That is, the denominator of the left-hand member of equation (11), $[H_2O]$, may be considered constant. Multiplying both members by the term $[H_2O]$ we obtain

$$[H^+] \times [OH^-] = K \times [H_2O] = K_w. \qquad (12)$$

This new constant K_w is called the ion product constant of water. It has been determined with considerable accuracy by a number of investigators and found to be very close to 1×10^{-14} at ordinary temperatures.

From (10) it appears that in pure water the concentration of hydrogen ion expressed in formula weights, mols per liter, must be equal to the concentration of hydroxyl ion similarly expressed: i.e. $[H^+] = [OH^-]$. In which case $[H^+]^2 = K_w$ or

$$[H^+] = \sqrt{K_w} = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}. \qquad (13)$$

The hydrogen-ion concentration of pure water is then 1×10^{-7} mols per liter.

Since the product of $[H^+]$ and $[OH^-]$ is equal to a constant it appears that acid and basic solutions differ in the degree by which one of the ions of water predominates over the other. It is also apparent that either the hydrogen-ion concentration or the hydroxyl-ion concentration will serve to define both acid and basic solutions. For instance, in a solution of sodium hydroxide containing $^1/_{100}$ mol of hydroxyl ion per liter, $[OH^-] = 1 \times 10^{-2}$. But from equation (8) $[H^+]$ must equal 1×10^{-12} in the same solution. Similarly in a solu-

tion of hydrochloric acid containing $\frac{1}{1000}$ mol of $[H^+]$ the $[H^+] = 1 \times 10^{-3}$ and the $[OH^-] = 1 \times 10^{-11}$. Since either the $[H^+]$ or $[OH^-]$ can be used to define adequately the concentration of acid and basic solutions there is no reason for using both. It is customary therefore to use the hydrogen-ion concentration only. The sodium hydroxide solution would be referred to as having a hydrogen-ion concentration of 1×10^{-12} and the hydrochloric acid a hydrogen-ion concentration of 1×10^{-3}.

The pH Scale.

The writing of very small quantities like .0000001 or 1×10^{-7} and .00000000001 or 1×10^{-11} is not convenient. To avoid this, mathematicians use the logarithm of the reciprocal of the number. Thus $\log \frac{1}{1 \times 10^{-7}} = 7$; $\log \frac{1}{1 \times 10^{-11}} = 11$; and $\log \frac{1}{0.576 \times 10^{-4}} = 4.24$. As a further simplification the term pH has been adopted as an abbreviation for the rather cumbersome phrase "logarithm of the reciprocal of the hydrogen-ion concentration," so that if we say a solution has a pH of 11 we mean a solution whose hydrogen-ion concentration is 1×10^{-11}. Likewise pH 7 means $[H^+] = 1 \times 10^{-7}$ and pH 4.24 indicates $[H^+] = .576 \times 10^{-4}$. Sørensen, in his early writings (*Biochem., Z.*, 21, 160), arbitrarily chose the symbol p_H as the exponent of the hydrogen-ion concentration. This symbol required a special character when printed and was inconvenient. The symbol pH is now almost universally adopted although a number of examples of transition stages in its evolution from the original symbol are still found in the literature.

In addition to the abbreviation affected by the use of the $\log \frac{1}{[H^+]}$ and the symbol "pH" there are other reasons for their adoption. The equation for calculating the hydrogen-ion concentration from the experimental data by which it is determined may conveniently be written with $\log \frac{1}{[H^+]}$ as the left-hand member. The solution of this equation gives the result as pH directly.

The pH scale furnishes a continuous scale for recording the hydrogen- and hydroxyl-ion concentrations in the most important range for biochemists, and for sanitary chemists as well, namely from $[H^+] = 0.1$ to $[OH^-] = 0.1$. On this scale a change in hydrogen-ion concentration from 0.001 to 0.01 (pH 3 to pH 2) is given equal weight with a

change from 0.000000001 to 0.00000001 (pH 9 to pH 8) although the latter is only one-millionth of the former. This is an advantage since in the reactions with which we are dealing the changes are of equal importance.

pH and "Alkalinity."

In discussing ionization and ionic reactions it was pointed out that the concentration of the ions was the important factor and not the concentration of the undissociated molecules. In the study of the chemical and biochemical reactions involved in water and sewage treatment, this is found true especially where the reactions of acids and bases are concerned.

As has been pointed out, acids and bases do not all ionize to the same extent. Hydrochloric, nitric and sulfuric acids, sodium, potassium and calcium hydroxides are all highly ionized while acetic and carbonic acids, hydrogen sulfide, and ammonium hydroxide are much less so. This situation makes necessary the use of two terms in describing the alkalinity or acidity of a solution. One term is a capacity factor and is a measure of the total amount of acid or alkali present, the other term is the intensity factor or the pH. The importance of these two factors may be shown by observing the properties of dilute solutions of hydrochloric, acetic, and boric acids of equivalent concentrations, e.g., one-half mol per liter. The hydrochloric acid burns the skin, the acetic acid has the pleasant sour taste of vinegar but smarts if a drop spatters into the eye, the boric acid has no sour taste and as is well known makes a good eye wash. Toward metals these acids exhibit a similar gradation of activity. The hydrochloric dissolves iron rapidly, the acetic attacks it slowly, while the boric acid is non-corrosive. Since these three solutions are of the same molar strength they have the same capacity factor but their respective pH values are approximately 0.3, 2, and 4.

Solubility Product Constant.

If the law of mass action be applied to a solution of a relatively insoluble substance like calcium carbonate a useful relation is developed. The calcium carbonate precipitates in the usual way $Ca^{++} + CO_3^{--} \rightleftarrows CaCO_3$ and the mass law equation is

$$\frac{[Ca^{++}] \times [CO_3^{--}]}{[CaCO_3]} = K \text{ (ionization)} \qquad (14)$$

Since calcium carbonate is present in the solid phase its concentra-

tion is constant, i.e., $[CaCO_3] = \text{const.}$ Multiplying both sides of equation (14) by the denominator of the left-hand term we have

$$[Ca^{++}] \times [CO_3^{--}] = K_{sol} \quad (15)$$

This equation will be found useful in the study of water softening reactions where the precipitation of certain constituents is sought.

For reasons which cannot be discussed here, the solubility constant rule (15), does not hold in relatively concentrated and complex solutions. But the concentrations met with in water treatment are small, so we may use the rule in its simple form.

Solutions of Constant Hydrogen-Ion Concentration.

(Reserve acidity or alkalinity, "Buffer Action.") Moderately dilute solutions of strong acids and strong bases are practically completely ionized. If then we add a certain amount of hydroxyl ion to a solution of a strong acid, hydrogen ion and hydroxyl ion will combine to form water and there will be a decrease in the hydrogen-ion concentration equal to the amount of hydroxyl ion added. If on the other hand we add more strong acid to the original dilute acid solution the hydrogen-ion concentration is increased in almost direct ratio to the amount of acid added.

Weak acids and bases such as acetic acid and ammonia are by definition those which are dissociated only slightly in moderately dilute solution. If we add hydroxyl ion to a solution of acetic acid for example, the formation of water with the hydrogen ion occurs as in the case of the highly ionized acids, but the undissociated acetic acid amounting to about 98 per cent of the total acid acts as a reservoir of reserve acidity and by ionizing forms more hydrogen ions to compensate for those used up in forming water. And if we add hydrogen ion it will combine with the acetate ion to form un-ionized acetic acid so that the hydrogen-ion concentration is not increased in proportion to the hydrogen ion added. If now we add sodium acetate (NaAc) to the solution of acetic acid the resistance to change of hydrogen-ion concentration is increased by increasing the amount of acetate ion as is shown below. (It should be noted that NaAc is highly ionized.)

(1) Addition of base

$$\begin{array}{ccccc} HAc & \rightleftarrows & H^+ & + & Ac^- \\ & & + & & + \\ NaOH & \rightleftarrows & OH^- & + & Na^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & H_2O & & NaAc \end{array}$$

(2) Addition of acid

$$\begin{array}{ccccc} HNO_3 & \rightleftarrows & H^+ & + & NO_3^- \\ & & + & & + \\ NaAc & \rightleftarrows & \downarrow\uparrow & & \uparrow\downarrow \\ & & Ac^- & + & Na^+ \\ & & HAc & & NaNO_3 \end{array}$$

From these reactions we see that the un-ionized HAc serves as reserve acidity furnishing H^+ as it is used up, while acetate ion acts as reserve alkalinity, combining with the added hydrogen ion to form HAc. If the resistance to hydrogen ion and hydroxyl ion are to be equal we should arrange to have the concentration of acetate ion equal the concentration of acetic acid. Since NaAc is almost completely ionized and HAc very little we may consider all the acetate ion as coming from the NaAc. So that a solution containing an equal number of molecules of HAc and NaAc will have equal reserve acidity and reserve alkalinity.

Inspection of the mass law equation

$$\frac{[H^+] \times [Ac^-]}{[HAc]} = K$$

brings out an interesting relation for a solution of equal reserve acidity and alkalinity. Such a solution is prepared so that $[HAc] = [Ac^-]$. Cancelling these terms we find $[H^+] = K$. Thus a solution of a weak acid and its salt prepared to have equal reserve acidity and reserve alkalinity has a hydrogen-ion concentration numerically equal to the ionization constant of the acid. If we wish to prepare a solution of constant hydrogen-ion concentration we pick an acid whose ionization constant is as nearly equal to the desired hydrogen-ion concentration as possible and mix it with an equivalent amount of its salt. The same reasoning applies to solutions of weak bases and their salts.

The phrases "reserve acidity and reserve alkalinity" are a little cumbersome and have not become popular. This property or action was early compared to a buffer or shock absorber, since such solutions were able to withstand the "shock" of added hydrogen ion or hydroxyl ion with comparatively little change in pH. As a result this action came to be known as "buffer action" and the terms "buffer," "buffer solution," "buffer substance," etc., have come into common use. A more precise term might have been chosen but "buffer" is now so generally used and with so definite a meaning that its adoption seems warranted.

Other types of substances will be met with which show buffer action. Solid calcium carbonate in a bacterial culture which is producing acid will be dissolved and will neutralize the acid as it is formed. Colloids

have a tendency to adsorb either hydrogen ion or hydroxyl ion and porous substances like charcoal have similar properties. A large body of water such as a reservoir or coagulating basin has, on account of its size, a sort of buffer action. The presence of buffer substances is sometimes desirable and sometimes undesirable in water and sewage treatment.

Isoelectric Point.

In a previous paragraph (p. 29) the existence of amphoteric compounds, i.e., compounds like aluminum hydroxide and many biochemical substances which ionize both as acids and bases, has been discussed. The chemistry of solutions of such compounds can be much more easily understood if we know under what conditions the acid ionization predominates and when the basic predominates. In other words we should be able to determine the "neutral point" of any particular ampholyte in order to work with it. This would be the point at which the degree of acid ionization equals the degree of basic ionization and is called the isoelectric point.

This isoelectric point may in simple cases be calculated from the law of mass action. In cases too complex for exact calculation the mass law is still of value as a guide to experimental studies of amphoteric compounds. Taking the simplest case, a compound HOR (R = any group) which is both monobasic and monoacid, we may write its ionization reactions

$$HOR \rightleftarrows R^+ + OH^-$$
$$HOR \rightleftarrows RO^- + H^+$$

and the mass law equations would be

$$\frac{[H^+] \times [RO^-]}{[HOR]} = K_a \qquad (16)$$

$$\frac{[R^+] \times [OH^-]}{[HOR]} = K_b \qquad (17)$$

substituting $\frac{K_w}{[H^+]}$ for $[OH^-]$ (see p. 32) equation (17) becomes

$$\frac{[R^+]K_w}{[HOR][H^+]} = K_b \qquad (18)$$

Since these two equations apply to the same solution, HOR in (16) is numerically the same as HOR in (17) and (18) and likewise $[H^+]$ in (16) is the same as $[H^+]$ in (17) and (18).

From the definition of the isoelectric point $[R^+] = [RO^-]$. That is to say, the number of positive and negative ions given off by the ampho-

teric substance HOR are equal. Dividing equation (16) by equation (18) and cancelling where possible we obtain

$$[H^+] = \sqrt{\frac{K_a}{K_b} \times K_w} \qquad (19)$$

This equation may be stated in words as follows: When the degree of acid and basic ionizations of an ampholyte are equal, the hydrogen-ion concentration expressed in mols per liter is numerically equal to the square root of the product of the ratio of the acid to the basic ionization constant multiplied by the ion product constant of water. From equation (19) we see that only when K_a equals K_b will the hydrogen-ion concentration at the isoelectric point be equal to 1×10^{-7} (pH 7) or the neutral point of pure water. If K_a is less than K_b the isoelectric point will be above pH 7 and when K_a is greater than K_b the isoelectric point will be below pH 7.

In a solution of an ampholyte an increase in pH increases the amount of negative ion or acid dissociation and causes a decrease in the basic dissociation. A decrease in the pH has the opposite effect, namely, to increase the basic and decrease the acid dissociation of the amphoteric substance. Inspection of equations (16) and (18) will serve to verify these observations. From the isoelectric point where the two dissociations are equal the increase in the one ion is more rapid than the accompanying decrease in the other so that the sum of the acid and basic dissociation is a minimum at this point.[3]

When as is frequently the case HOR is less soluble than any of its salts the isoelectric point will be the point of minimum solubility.

Unfortunately the calculation of the isoelectric points of substances which are capable of giving off more than one acid or one basic ion requires more data and labor than does the experimental determination of the minimum point for conditions to be met. The calculations given above have been of value in disproving the popular assumption that the neutral point of pure water is the neutral point for all other substances and the demonstration of the conditions existing at the isoelectric point is very helpful as a guide in investigations of such complex systems as sludges and alum floc even though the isoelectric point cannot be calculated with any certainty.

[3] If in equations (16) and (18) we let $X = R^+ + RO^-$, and solve for X we find by the usual method of differential calculus that X is a minimum when $[H^+] = \sqrt{\frac{K_a}{K_b} \times K_w}$. This is also the point according to equation (19) where $[R^+] = [RO^-]$. Also if the curves for the dissociations of HOR as acid and as base are plotted assuming any probable values for K_a and K_b the undissociated HOR will be seen to be a maximum where $[R^+] = [RO^-]$.

Chapter II.

Colloids.

Our discussion of chemical theories which bear upon the problems of water and sewage treatment would be incomplete without a consideration of the subject of colloids. In fact the handling of colloids is one of the first things a sanitary chemist has to learn.

The treatment of the subject of colloids historically has tended to over-emphasize the erroneous notion that colloids and crystalloids are two different classes of substances. We shall therefore begin with a discussion of the preparation and distinguishing characteristics or properties of colloids.

If we prepare a series of suspensions of coarse sand, fine sand, and powdered sand in water we note that the coarser particles settle out very rapidly and the finer particles more slowly. If the sand is ground very fine indeed we can obtain a suspension which apparently does not settle out in the course of several days. These stable suspensions cannot ordinarily be clarified by filtering through fine filter paper, and if viewed under the microscope the individual particles would be too small to be distinguished. If the amount of powdered sand in the suspension is relatively small the mixture may appear to be perfectly clear when held toward the light. But if a beam or pencil of light is passed through the suspension at right angles to the line of sight (Fig. 2) the preparation appears milky, clearly showing that we have a suspension and not a true solution. Such a preparation which is "almost a solution" is an example of a colloid. The turbid path of a beam of light applied as above is called a "Tyndall cone" and is characteristic of colloids in general.

If we attempt to make suspensions of ordinary salt in water we find that it is too soluble, but if some liquid like benzene, in which salt is insoluble, is used we can obtain permanent preparations of colloidal salt in benzene similar to those of sand in water. In fact by properly choosing the liquid and the method of subdividing or "dispersing" the solid we can produce any substance in a colloidal condition.

There is much more to the colloidal condition than merely the degree

of subdivision. Colloidal preparations made by finely dividing a substance in a liquid are not very stable but will coagulate and settle out in a few days. The particles in truly permanent colloidal preparations, such as are frequently found in nature or may be prepared in the laboratory, have either picked up and combined with a small amount of some soluble substance, or their own molecular structure will be found to contain a soluble group. These soluble groups or substances constitute

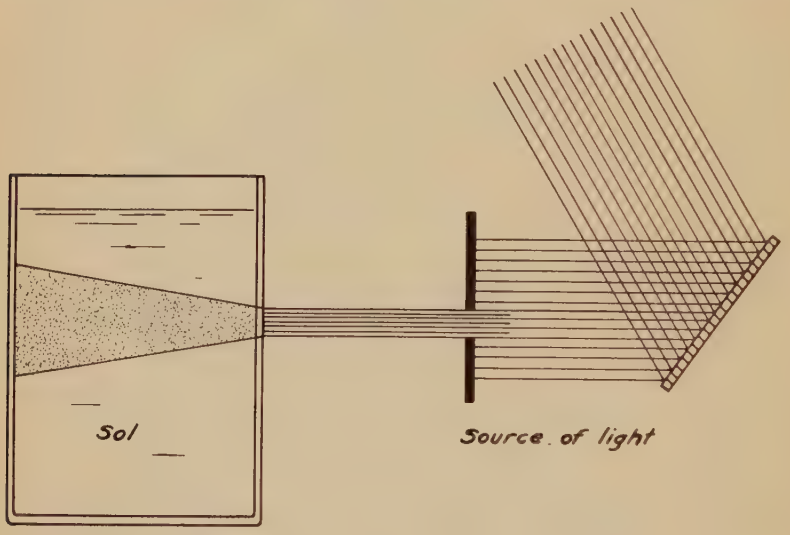


FIG. 2.—Tyndall Cone (after Bary).

"links" between the insoluble portion and the solution and account in large measure for the stability of colloids. The presence and character of these "solution links" [1] will be noted throughout the chapter.

The particles in these colloidal preparations are not definite chemical substances like sugar or salt. For example, Thomas [2] suggests $X\ Fe_2O_3$, $W\ H_2O$, $Y\ FeCl_3$, $Z\ FeCl_2^+ + Z\ Cl^-$, as the formula for so-called "colloidal iron." (The $FeCl_3$ is the solution link.) While there is a relation between the properties of the colloid and the values of W, X, Y and Z it is not defined with the exactness that we find in the relation between the composition and properties of pure chemical substances. Such preparations are sometimes referred to as "colloidal solutions," but the term is cumbersome and in some ways contradictory. The term

[1] This conception was first suggested by Thomas. Thomas & Frieden, *J. Am. Chem. Soc.*, **45**, 2522 (1923).
[2] *Loc. cit.*

"sol" is rapidly coming into general use and fills a real need for a special term. True solutions of pure chemical substances are regarded as being composed of particles of uniform composition and of the same general size as the molecules of the solvent and it is for such examples that the name "solution" should be reserved. Naturally, the smaller the particles are, the more likely they are to be composed of only one kind of chemical molecules, so that there will be a gradual gradation from colloids to true solutions.

Examples in which the solid is so coarsely dispersed that it settles out readily are referred to as "suspensions." The three terms, suspensions, sols, and solutions are thus used to differentiate progressively finer degrees of dispersion of substances, presumably suspended in liquids. Naturally the limits of the zones to which these terms apply must be determined largely on arbitrary grounds.

For convenience, the dimensions of small particles are given in microns for which the abbreviation is the Greek letter mu—μ. One micron equals one one-thousandth of a millimeter (1 μ = 0.001 mm.). The millimicron (mu mu) which is one-thousandth of a micron or one-millionth of a millimeter, is also useful. Since one millimeter equals one twenty-fifth of an inch, 1 μ = 1/25000 inch and 1 μμ = 1/25,000,000 inch.

The limit of the resolving power of the compound microscope has been suggested as an approximate upper limit for colloidal particles. Since this is in the neighborhood of 1 μ, the round number has been chosen. This is approximately the size of particles which may be prevented from settling by a weak solution link (e.g., gold or platinum sol particles). Particles of this size will pass through most paper filters and in many ways exhibit properties different from those of suspensions. The choice of one micron as the limit between the size of particles in suspension and sol particles or colloidal particles, while arbitrary, appears reasonable.

The lower limit of the size of colloidal particles should differentiate them if possible from true molecules, but molecules are of widely different sizes. Although one millimicron is less than the diameter of some particles found in systems[3] which we have commonly considered true solutions, it has been chosen as the lower limit of the size of colloid particles. A hydrogen molecule is estimated to be 0.10 μμ in diameter, a sodium chloride molecule 0.26 μμ, and a molecule of cane sugar 0.7 μμ. When the particles are smaller than 1 μμ the Tyndall cone is no longer seen with ordinary illumination.

[3] A *system* includes all of the substances taking part in a reaction.

Sols then include systems in which there are particles of from 1 μμ to 1 μ diameter held in suspension in some liquid [4] by "solution links."

In discussing colloids we shall find it convenient to refer to the substance in the finely divided condition as the *dispersed phase* [5] and the liquid as the *continuous phase.* (A number of synonymous terms are in common use, e.g., dispersed phase = internal phase = micelle; and continuous phase = external phase = dispersion medium.)

Kind of Colloids.

We have already defined a sol. The definition should be further modified to differentiate sols from gels. When the number of disperse particles per given volume become so great that they touch or nearly touch, the system will no longer flow, is no longer liquid, and is then called a *gel.* No sharp line of demarkation between sols and gels has been established and such a limit would probably not be very useful. We have no difficulty in deciding that Missouri river water is a sol and that alum floc is a gel. The most common liquid colloids, sols, may for convenience be classified [6] as follows:

Sols
- Endo solution link
  - (*a*) *Suspensoids,* weak solution link
  - (*b*) *Emulsoids,* strong solution link
- Exo solution link
  - (*c*) *Protected colloids,* suspensoid sols plus protecting agent
  - (*d*) *Emulsions* (two immiscible liquids plus an emulsifying agent)

This classification gives two subdivisions and four classes of sols. The two classes, (*a*) suspensoids and (*b*) emulsoids, include systems in which the dispersed phase and the continuous phase are the significant components and the solution link is part of the makeup of the colloidal substance. In the third and fourth classes, (*c*) protected colloids and (*d*) emulsions, a third component, an added stabilizing agent or "solution link," is essential.

(*a*) **Suspensoids.**—The simplest class is that in which the dispersed phase combines with or reacts with the continuous phase to only a small

[4] In this discussion we frankly ignore those cases in which colloidal particles are dispersed in a gas (smoke) and those in which colloidal particles are dispersed in solids.

[5] A *phase* is any portion of a system separated by a definite physical boundary from the rest of the system. The three physical phases are solid, liquid and gas. Several liquid phases and several solid phases may be present in the same system. Oil and water together form two liquid phases; if ground quartz and ground limestone are mixed in there will be in addition two solid phases.

[6] It must be borne in mind that such classifications are artificial and arbitrary and that cases are sure to occur which do not fit perfectly into the scheme.

extent. If gold is broken up very fine in pure water we have an unstable gold sol, but if a small amount of salt is present a little gold salt is formed which combines with the particles and forms a solution link. If oil is shaken up vigorously with pure water (no soaps or similar substances present) we can produce an oil sol composed of minute globules of oil in water. Such sols as the two just mentioned are commonly referred to as suspensoid sols. Less common terms which are nearly synonymous are non-solvated sols, lyophobic sols and irreversible sols.

(*b*) **Emulsoids.**—The second class is that in which the substance of the dispersed phase combines to some extent with the continuous phase. This compound furnishes a relatively strong solution link. If gelatin or agar or starch is placed in water it combines with the water slowly but steadily, becoming first soft and gelatinous and finally liquid. With a very little encouragement, such as stirring and warming, these substances form sols with great ease. A large number of biological and organic substances, such as soap, peptone, albumin, gelatin and other proteins, belong in this class. Also we have some inorganic sols in which the dispersed phase is combined with water. "Colloidal iron" is ferric hydroxide which is combined with some soluble ferric salt to act as a solution link. Some clays appear to belong in this rather than in the suspensoid class. This class is referred to as emulsoid sols. Common synonyms are lyophilic sols, solvated sols and reversible sols.

Although we are primarily concerned with systems in which water is the continuous phase it is interesting to note that rubber behaves in benzene much as gelatin behaves in water.

In suspensoid sols and emulsoid sols there are in each case two significant substances present, the dispersed substances and the dispersion medium. There is another group of sols in which an appreciable amount of a third substance must be present. This third substance must be one which has a tendency to combine with or dissolve in both the continuous phase and the colloid particles so that it may form a "double solution link." These may be called stabilized sols since they are in most cases more stable than suspensoids or emulsoids. This group may be further subdivided into two classes: (*c*) stabilized suspensoids which are commonly referred to as "protected colloids" and (*d*) "emulsions" in which two liquids and a stabilizing substance are involved.

(*c*) **Protected Colloids.**—If some gelatin is added to a silica sol or a gold sol it is found to be very much more difficult to coagulate or precipitate the silica or gold than if the gelatin were not present. The gelatin forms a film about the colloidal particles and protects them

from the action of precipitating agents, and, since the film is soluble, the particle is held up. In a similar way many forms of organic matter will stabilize the turbidity in water or sewage, making clarification difficult. This effect is taken advantage of when the formation of boiler scale is retarded by the use of organic substances which retard precipitation. These examples serve to illustrate what is meant by protected colloids.

(*d*) **Emulsions.**—The term "emulsion" is in common use and its popular definition is not very far from the definition to be used here. Considerable confusion will be avoided if only those systems are called "emulsions" which consist of two immiscible liquids, one dispersed in the other with the aid of a third substance, an emulsifying agent.

The common example is the emulsion of *oil* in *water* with the aid of ordinary sodium or potassium soap. Butter fat is emulsified in milk with the aid of the milk protein. Emulsions of *water* in *oil* can be made by using calcium or magnesium soaps. Since both sodium and lime soaps are present in sewage, the latter especially in hard water regions, there is ample opportunity for the formation of emulsions.

It is worth while to note that both the protecting agents in the case of protected colloids, and the greater number of emulsifying agents in the case of emulsions, belong to the class of emulsoid colloids. They owe their protecting or emulsifying power to an affinity for the solvent on the one hand and for the dispersed substance on the other.

Properties of Colloids.

One difficulty in the study of colloids is that there are relatively few properties exhibited by all classes of sols alike. Probably the most important and most general characteristic is that of large surface per unit volume. A cube of quartz 1 cm. on a side would have an area of 6 sq. cm. If it is broken up to a rather fine sand each grain of which is a cube 0.1 mm. on a side all the grains will have a total area of 600 sq. cm. But if it is further broken up so that the grains become colloidal in size the total area will be from 60,000 to 6,000,000 sq. cm. depending upon the exact degree of subdivision. With this enormous surface in contact with the liquid it is to be expected that reactions will take place in sols which would not occur in suspensions.

The size of colloid particles falls within a common range; they are all non-homogeneous systems, and exhibit a Tyndall cone; they are not pure chemical compounds and hence in their reactions they do not follow the ordinary quantitative chemical laws; in the chemical complex composing the particle, there is always a soluble salt or group which

acts as a solution link. Beyond this we cannot go in naming general properties of colloids. Further discussion must be by classes.

Properties of Suspensoids.

Some of the most important properties of suspensoids may be best observed by means of the ultramicroscope. This instrument is merely a device for producing a Tyndall cone so that it may be viewed through a microscope. This is best done when the axis of the microscope forms a right angle with the beam of light.

If the suspensoid sol is then examined under an ultramicroscope the individual particles are seen as points of light dancing about in an irregular manner. This is known as the Brownian movement and is caused by the impact of the molecules of the liquid on the particles. The rate of sedimentation of the colloidal particles, which figured from Stokes' law would be very slow, is obviously further retarded by the Brownian movement.

If plus and minus electrodes are introduced into the sol at opposite sides of the microscopic field the particles will continue their zigzag motion but will also move slowly toward one electrode or the other. The conclusion is that the particles are electrically charged, hence their movement under the influence of applied electrical potential. This migration of sol particles with the electric current is commonly called cataphoresis, though electrophoresis is a better term. From the direction of their migration it is found that in a given sol all particles carry a similar charge and that the majority of suspensoid sols in water are negative. Sols of iron and aluminum oxide (and of several dyes) are positively charged.

The two most probable sources of the charge appear to be (1) adsorption [7] of ions of one sign on the particles; and (2) ionization of

[7] Adsorption is the tendency to concentrate a constituent of a phase at its boundary with another phase. The amount of adsorption is greater, the greater the area of the boundary surface. Thus charcoal, which is very porous, is a very active adsorbent for both gases and substances in solution. Since the disperse phase of a colloid has such an enormous surface, it is obvious that adsorption plays an important part in colloid chemistry.

There appear to be several possible causes for this tendency to concentrate at a boundary surface. It has been shown by Gibbs by mathematical methods that if a dissolved substance tends to decrease the surface tension, it will become more concentrated at the surface than in the body of the liquid, and that if it increases the surface tension it will be less concentrated at the surface. This undoubtedly explains certain cases of adsorption. In other cases there is evidently a force exerted by the molecules of the phase on the other side of the boundary. This force may easily be chemical in nature; that is, similar to the valence forces which hold atoms together in molecules. Reference to the discussion of valence (p. 20) will indicate further how adsorption combinations may be formed.

some of the molecules of the colloid particles, producing ions of one sign which diffuse away from the particle while the corresponding ions of opposite signs are held fixed.

There is always a small amount of electrolyte present in any sol to furnish the ions for charging the particles; in fact it is impossible to make a suspensoid sol without a small trace of some electrolyte present. Some particles apparently secure their charge by adsorbing negative ions (either OH^- or some other anion) from the solution, and positively charged particles are those which adsorb positive ions.

There may be some chemical reason why some kinds of particles prefer negative ions and some positive, or the charge may be dependent upon the relative concentration of the ions. In some cases we can reverse the charge by changing the relative concentration of the ions. Addition of aluminum ion will at first slow down the rate at which certain negative particles travel with the electric current and further addition will cause the particles to travel in the reverse direction, showing that they have become positively charged. The *concentration* of the oppositely charged ions at which particles change their charges is called the *isoelectric point.* (This definition of isoelectric point suits the case for suspensoid colloids and though different in some respects from the one already given (p. 37) for proteins, is not necessarily in conflict with it.) When the charge on a colloid particle is due to OH^- or H^+, its conditions will be determined by the hydrogen-ion concentration.

The second way in which a particle can acquire a charge, namely by partial ionization, is easily pictured. If the molecules on the outside of a ferric oxychloride particle should partially ionize as follows

$$X\,Fe(OH)_3\ Y\,Fe(Cl)_3 \rightarrow X\,Fe(OH)_3 . Y\,FeCl_3 . Z\,FeCl_2^+ + Z\,Cl^-$$

the Cl^- ions would undoubtedly diffuse away from the particle while the $Fe(Cl)_2^+$ residues would remain on the particle and the latter would be positively charged.

The three characteristics of suspensoids, size, Brownian movement and solution link (i.e., soluble ions), all tend to stabilize these sols, that is, to prevent their settling out.

The electrical charge indicates that the particle as a whole acts in some respects like an ion and may be referred to as a colloidal ion. As would be expected it can react with oppositely charged ions to form insoluble salts or un-ionized compounds. Such reactions usually result in coagulation through the destruction of the soluble portion of the colloidal particle which we call the "solution link." This precipitation

reaction is frequently referred to as the neutralization of the charge of the colloidal particle by an oppositely charged ion, and the reference is made in a hazy sort of way which leaves the reader in doubt as to whether the reaction is similar to ordinary reactions between ions or something special. It is apparently an ordinary ionic reaction.

The stability of suspensoid sols is often attributed in part to the repulsion resulting from the electrical charges. Thomas,[8] Porter and Hedges[9] and Smoluchowski[10] have pointed out that this cannot be so. For example, in the case of the iron oxychloride sol mentioned above it is true that the $FeCl_2^+$ ion gives a positive charge to the colloid particle but the Cl^- ion is not far away, so that the system as a whole is electrically neutral.

Preparation of Suspensoid Sols.

Such questions as the conditions under which the turbidity in water becomes so highly dispersed, and the factors tending to produce magnesium hydroxide in a colloidal rather than a granular condition in water softening, are best understood after a brief general discussion of the question of the preparation of suspensoids.

Suspensoids may be prepared by pulverizing larger particles of the substance in the presence of the proper electrolyte until they reach colloidal dimensions, or by precipitating the substance from solution under such conditions that the particles do not become larger than the colloidal size. The first is called the dispersion method, the second the condensation or precipitation method.

In the dispersion method the principal essential is the proper method of application of sufficient mechanical force. It also is necessary to provide for the presence of a small amount of some salt so that its ions may furnish the necessary electrical charge. (Natural waters and some grades of distilled water usually contain enough electrolyte for this purpose.) The mechanical forces of nature, acting as they do over very long periods of time, are very effective in reducing rocks and soils to such a fine state that they are easily carried off by streams as very stable suspensoid sols.

The forces operating in the condensation or precipitation method, which determine whether a given precipitate will tend to be colloidal or not, are more chemical in nature. Von Weimarn has suggested the following picture of what happens during precipitation. The first step

[8] *Loc. cit.*
[9] *Phil. Mag.* **44**, 641.
[10] *Z. Physik. Chem.* **92**, 129.

is the combination of the ions of the insoluble substance (e.g., $Al^{+++} + 3OH^- \rightleftarrows Al(OH)_3$). This combination is practically instantaneous or at least it is more rapid than any other reaction which might be used to measure its speed. The next step is the formation of micro-crystals by the coming together of several molecules. These crystals will be variable in size but of colloidal proportions. The rate at which these micro-crystals form will be greater, the greater the number of insoluble molecules (i.e., the supersaturation), and will be less the greater is the solubility of the particular substance.

From this point an increase in size may occur in two ways: (1) recrystallization, that is the growth of larger crystals at the expense of smaller ones, and (2) by the clumping or aggregation of a number of small crystals to form a larger group.

The rate at which recrystallization or crystal growth takes place will be greater (1) the greater the solubility (i.e., the concentration between crystals); (2) the greater the number of crystals or the crystal surfaces; and (3) the greater the diffusion coefficient.

Since colloidal particles do not diffuse as molecules do, the chance of increasing the number of contacts between particles, and hence the rate of aggregation, depends upon stirring either mechanically or by local application of heat to cause convection currents.

From the above presentation of the successive steps in precipitation and the forces affecting the speed of these steps, we may formulate a series of rules for the preparation of colloids:

Let R_f = rate of formation of original micro-crystals
R_g = rate of growth of crystals (i.e., recrystallization)
R_a = rate of clumping or aggregation
S = solubility of precipitating substance
X = amount of precipitating substance present in excess of its solubility

It is obvious that if R_f is greater than R_g and R_a the substance will precipitate in, and remain in, the colloidal state for an appreciable time. If R_g and R_a, one or both, are greater than R_f then the colloidal state will be transient or may never appear.

Keeping in mind the factors affecting these rates mentioned above, we may determine their probable relative value as follows:

When R_f is large, then a large portion of the substance being precipitated will soon be found in a colloidal state of dispersion. If R_f is large due to a large X, there will be a large number of particles and hence a concentrated sol. In this case R_a may be large, due to the number of crystals, and the practically unavoidable thermal stirring may

cause the sol to coagulate or form a gel; or if S is relatively large, R_g may be large enough to cause the crystals to grow above colloidal size in a short time.

If R_f is large due to a very small S (N being moderately large), then R_g is bound to be small and the crystals of colloidal dimensions will not grow; further there will not be a great many of them, so the tendency to aggregate (R_a) will be small. The chances for a stable sol under these conditions are good.

When R_f is small, it will usually be equal to or smaller than R_g, especially if S is large. Under these circumstances the colloidal condition will not be observable.

When S is very small, as in the case of aluminum hydroxide recrystallization does not take place even when the micro-crystals of colloidal size are collected together into aggregates. A number of gel flocs result instead of a crystal.

Precipitation of Suspensoids.

From the foregoing discussion it appears that the precipitation of a substance in colloidal form can in large measure be controlled by the concentration of the solution in which it is produced. Once an undesirable colloid is formed it may best be destroyed by counteracting the forces tending to stabilize the sol. Of these, the most easily neutralized in most cases is the "solution link." An experiment will best illustrate how this may be done. If to a series of test tubes, each containing 10 cc. of some negative sol like gold or arsenious sulfide, different amounts of some salt like sodium chloride are added, it will be found that all the samples to which more than a certain amount of salt has been added will coagulate in a relatively short time, while those with less than the critical amount of salt will be unaffected.

This critical coagulating or precipitating concentration of the salt will vary with the kind and sample of sol and the time one sets between addition of salt and moment of observation, but the most marked variation is with the valence of the effective ion. From ordinary chemical reactions we would expect that it would take one-half as many divalent calcium ions (Ca^{++}) to precipitate a given negative sol as the number of monovalent sodium ions required, and one-third as many trivalent aluminum ions (Al^{+++}). Experiment shows, however, that the precipitating efficiency of ions on colloids increases out of all proportion to the increase in valence. In one case, for example, the amounts of Na^{+}, Ca^{++} and Al^{+++} required to precipitate a given sol stood in the ratio 500 : 7 : 1. In these precipitation reactions the amounts of

the reacting salts, which are carried down in the precipitate, are chemically equivalent (i.e., 1 $AlCl_3$: 1½ $CaCl_2$: 3 NaCl). These data are in accord with experience in water treatment which has shown that very small amounts of alum are effective in clarifying water.

There are two possible ways in which these salts may break the solution links: (1) One ion of the added electrolyte may combine with the oppositely charged ion of the solution link, forming an insoluble compound; or (2) the added electrolyte may "salt out" the colloid. This "salting out" effect is well known in many fields; e.g., oxygen is much less soluble in sea water than in pure water and, in fact, dissolved oxygen may be determined quantitatively in water by adding certain salts to the sample and analyzing the gases which are evolved.[11] The salting out effect increases greatly with the valence of the salt ion whose charge is opposite to the colloid ion, and decreases with the valence of the salt ion of like charge to the colloid ion. In salting out a negative sol, therefore, ferric or aluminum chloride would be much more effective than calcium or magnesium chloride, and the chlorides would also be more effective than the corresponding sulfates.

Positively charged sols are precipitated by negatively charged anions in a similar way and the same effect of valency holds as held for the precipitation of negatively charged sols by kations. With the exception of ferric hydroxide sol positive colloids are comparatively rare in natural waters, though in trade wastes they are present at times. The effect of the divalent sulfate radical (SO_4^{--}) of "alum" undoubtedly assists in clearing up such liquors in a way which is seldom appreciated.

Properties of Emulsoids.

Emulsoids or "lyophilic colloids" have, as their second name suggests, a considerable affinity for the solvent. That is, they contain a large number of soluble groups in their chemical makeup which act as solution links. As a result the dried substances become dispersed easily and form stable sols frequently of high concentration. The sol particles take up water during dispersion and attain practically the same index of refraction and specific gravity as water or the dilute solution which is the continuous phase.

In these two important respects, index of refraction and extensive combination with the solvent, emulsoids differ generally from suspensoids. (Individual exceptions to this generalization exist.) The small difference in refraction of light between the disperse and con-

[11] Becker, H. G., *J. Soc. Chem. Ind.* **42**, 484-6 (1923); *Sci. Proc. Roy. Dublin Soc.* **17**, 249-253 (1923).

tinuous phases makes it impossible to distinguish individual particles under the ultramicroscope. The Tyndall cone is observable but it appears under the microscope merely as a haze. Hence this very useful research tool is useless with this class of colloids.

The small difference in specific gravity between the sol particles and the continuous phase is an important factor in increasing the stability, or apparent stability, of emulsoid sols. The particles might clump together to form aggregates considerably larger than colloidal size without much apparent separation of the two phases. It is not sufficient then in the case of emulsoids to cause clumping of particles in order to destroy the sol. Some agent, chemical or physical, must be used which will remove from the particles the water which they took up during dispersion. Dehydration or desolvation appears to be the necessary preliminary step in flocculation.

Flocculation from an emulsoid sol is not a sharply defined change as it is in the case of suspensoids. In most cases there is a gradual change in viscosity as the particles lose water, become clumped together and finally separate out or "set." That is, flocculation is the reverse of swelling or dispersion. The effects of a given salt on the viscosity, swelling and flocculation of an emulsoid will be parallel. A separate discussion of these properties is therefore not necessary. For the purpose of this discussion one effect may be predicted from either of the others, since all three depend upon the amount of water which the particles take up.

Gelatin and other proteins being amphoteric substances are very sensitive to the hydrogen-ion concentration (p. 37). At their point of minimum ionization, the isoelectric point, they combine with or take up water to the least extent. Adjustment of the pH to the isoelectric point would therefore assist in coagulating a gelatin sol. The addition of certain soluble salts tends to dehydrate emulsoid particles, as does also the addition of some other liquid like alcohol which has considerable affinity for water and little or none for the emulsoid. Dehydration, if carried far enough, causes the sol to coagulate. As would be expected the effect of dehydrating agents appears to be greatest at the isoelectric point of protein sols.

The effect of ions on the swelling, viscosity, etc., of proteins seems to be of two kinds. The first is the direct effect of the charge of the ion on the charge of the colloid, similar to the effect of ions on suspensoids. In such cases the valence of the ion appears to be the important factor, and we find the tri- or tetravalent ions a great deal

more effective than divalent ions, and the monovalent ions still less effective.

The second effect is best described as a competition between the colloid particles and the ions of the electrolyte for water molecules. The fact that ions tend to take up, or draw toward themselves, molecules of water when in solution has been recognized for a number of years, and experiments have been carried out to determine the relative strength of this tendency for different ions. If a series of ions is arranged in the order in which they tend to precipitate proteins, they will be found to be in the order of their relative tendency to become hydrated, e.g., SO_4^{--}, Cl^-, Br^-, I^-, SCN^-. This lyotropic or hydration effect is observable in rather concentrated solutions (1 *N* or more), and hence is out of the range of concentrations ordinarily met with in water and sewage treatment.

Another ion effect must be borne in mind in dealing with emulsoids, namely, the Donnan membrane equilibrium. This is a theorem derived to show that when one ion of a system containing salt is held fixed, either by a membrane or some other force, there results an unequal distribution of the mobile ions and hence an osmotic pressure is produced. Proteins, as has already been observed, are amphoteric electrolytes which ionize to give a mobile hydrogen ion or hydroxyl ion, or in the case of their salts a chloride ion, sulfate ion, etc., and an immobile ion, the protein residue, whose immobility is caused by its size and attachment to the main body of the colloid particle. A particle of gelatin, therefore, tends to acquire a larger number of mobile ions than the liquid which surrounds it. These ions on account of their osmotic pressure draw water molecules into the gelatin particle and as a result the particle swells. The difference in ionic concentration also produces a "concentration cell," whose voltage is dependent on the ratio of these differences. There is no uniformity of opinion as to the significance of this "Donnan equilibrium voltage." It was suggested as an explanation of the charge on the particle, but this cannot be. The Donnan equilibrium shows an excess of *mobile* ions on one side of the membrane, but the total plus and minus charges including the fixed protein ions must be equal. The charge on the emulsoid particle which determines the direction and velocity of its movement with an electric current must be independent of the Donnan effect and must, as in the case of the suspensoids, depend upon surface adsorption of ions or an ionization of the colloid material. Swelling alone can be explained by the Donnan effect.

So it appears that the important properties of emulsoids from both the theoretical and practical standpoint are intimately connected with the one question of the combination of sol particles with water. Attention has been called (p. 60) to the fact that the water molecule has ample means for combining with a variety of substances, either positive or negative, through either its exposed pairs of electrons or by using its hydrogen atoms as bonds ($H:\ddot{O}:H$). The amount of water held by these sol particles is frequently very large, not infrequently three to ten times their own dry weight. The pressures required in filter pressing many sludges indicate that the water is held in more than a mechanical way. In fact some evidence [12] indicates that every water molecule in a 10 percent gelatin sol is held in some way by the gelatin molecules. Under the topic "Sludge Drying" the question of this combination with water will be further discussed.

Properties of Exo-linked Colloids.

It is difficult to assign any common property to this class beyond that already mentioned in the description of the class; namely, that they are not easily coagulated due to the presence of a lyophillic colloid which acts as a stabilizing agent. Each particular example will have its own properties depending upon the particular substances of which it is composed. As might be expected reagents which attack the stabilizing agents will tend to destroy the sol. For example, proteins which have been partly broken down through chemical or physiological action are not as effective stabilizing agents as those in normal condition.

Properties of Protected Colloids.

The first class—the protected colloids—are characterized, like the suspensoids from which they are prepared, by a comparatively low concentration. The effect of the stabilizing agent is to form a viscous film about the individual particles and thus greatly retard growth of particles by recrystallization (p. 48). On account of their relative lack of sensitiveness to small concentrations of ions these stabilizers inhibit the action of salts on the suspensoid particles without themselves being coagulated. It would be advantageous if we had more specific data on the degree to which certain substances inhibit the precipitation of calcium carbonate, magnesium hydroxide and aluminum hydroxide especially.

[12] Coblentz, "The Rôle of Water in Minerals," *J. Frank. Inst.* **172**, 309 (1911).

Preparation and Properties of Emulsions.

By far the greatest number of common emulsions have some sort of a solvated colloid for the emulsifying agent.

The emulsions of mineral oil in water produced by the action of soap are among the most common. Apparently the soap has a double action in stabilizing emulsions. It increases the viscosity of the external or continuous phase, thus lessening the tendency of the oil globules to rise, but, what is more important, it greatly decreases the surface tension at the surface between the external liquid and the oil globules. A great deal of energy is required to break a liquid into fine globules and this energy, or a large portion of it, is located on the surface of the globules as surface tension. When two globules combine to form one, there is a decrease in total surface and a corresponding decrease in energy. In other word, surface tension is a force which tends to cause globules to coalesce. Any reagent then which decreases surface tension will tend to stabilize emulsions.

Theories have been suggested to explain just how these stabilizers affect the surface tension, and also why some emulsifiers produce oil-in-water emulsions and why some produce water-in-oil emulsions.[13] For practical purposes it is sufficient to say that if the emulsifying agent is soluble in water then water will be the external phase (i.e., oil globules will be emulsified in water); but if the emulsifier is soluble in oil and not in water, then globules of water will be emulsified in the oil and oil will be the external phase.

For example, ordinary soap (largely sodium or potassium stearate and oleate) is soluble in water and will emulsify petroleum oil in water very successfully. Calcium and magnesium soaps are insoluble in water but are soluble in petroleum oils. If calcium chloride is added to an emulsion of oil in water which has been stabilized with a sodium soap, the insoluble lime soap is formed and the emulsion is broken. On shaking the mixture the lime soap dissolves in the oil and proceeds to emulsify the water in the oil. The emulsion has thus been inverted from oil in water to water in oil.

There is a less common type of emulsion in which the stabilizing agent is a very fine insoluble powder, like silica, barium sulfate, charcoal, etc. These powders seem to owe their stabilizing action to the fact that the two liquids do not have the same tendency to wet the powdered particles. Water will wet clean glass but will run off if the glass is the least bit greasy. Mercury on the other hand will not

[13] Finkle, Draper & Hildebrand, *J. Am. Chem. Soc.* **45**, 2780.

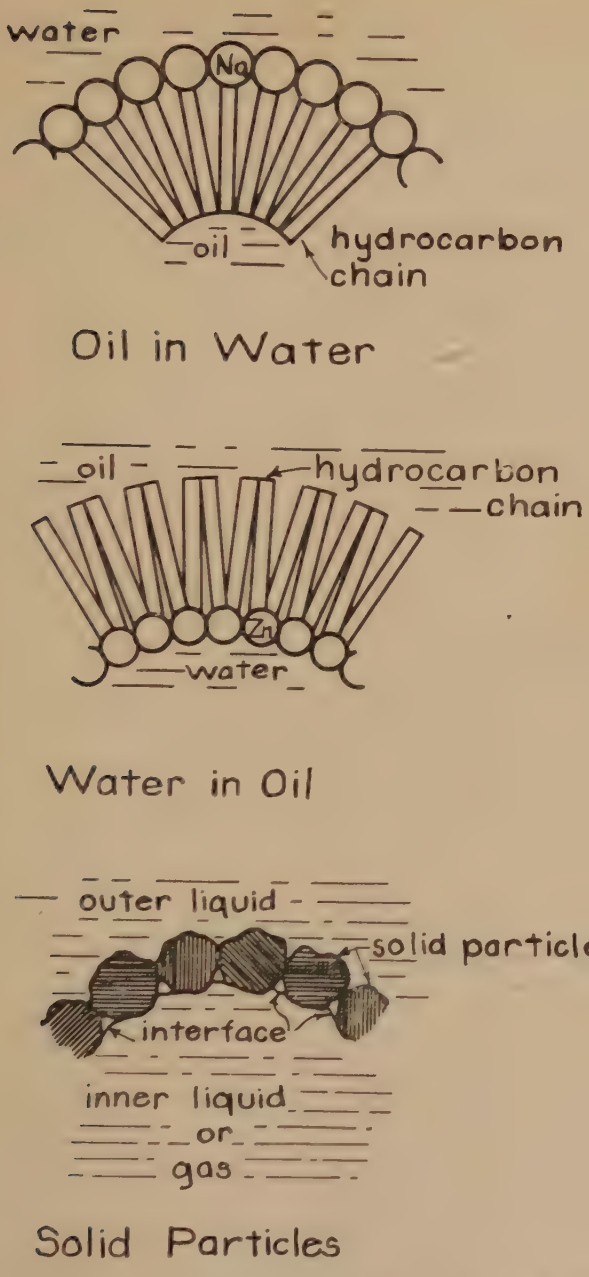


FIG. 3.—Stabilization of Emulsions (after Finkle, Draper & Hildebrand).

wet glass but tends to draw away from it. Between these two we have any number of intermediate tendencies of liquids to wet solids. If, then, two immiscible liquids *A* and *B* are shaken up with a finely powdered substance the following results are possible: (1) If one liquid has a strong tendency to wet the solid and the other liquid has little or no such tendency, the solid will be found entirely within the liquid by which it is wet and no emulsion will result. (2) If liquids *A* and *B* each have exactly the same tendency to wet the solid no emulsion will be produced and the solid will be found at the boundary surface between the two liquids. This case is rare. (3) The third possibility is the one in which we are interested; namely, if both of the liquids wet the solid but *A* has a greater tendency to do so than *B*, the solid particles will collect at the surface between the two liquids, but there will be a crowding of the particles toward liquid *A*. This will cause the boundary surface to bend so as to be convex toward *A*. As globules of *B* are formed during the shaking this tendency of the surface to curve will prevent the coalescence of the globules of *B* and an emulsion will be formed. This may be summarized in a simple rule, namely, that a powder will stabilize an emulsion of two liquids if both tend to wet it, and the liquid having the greater tendency to wet the solid powder will be the external phase.

A somewhat similar effect of finely powdered solids will be noted in the discussion of foaming of steam boilers.

Breaking of Emulsions.

From the discussion of the preparation and properties of emulsions it is evident that one of the surest ways to break an emulsion is to destroy the emulsifying agent. When milk sours, the proteins, which stabilize the butter fat as cream, are altered so that they no longer function. Agitation (churning) then causes the fat globules to collect as butter. The nature of the emulsifying agent is not definitely known in all cases and even where known it is not always as easily attacked as it is in the case of cream. There are, however, two remaining methods of attack, namely, to offset the effect of viscosity or to increase the surface tension. The effect of viscosity may be offset by change in temperature or by the addition of some reagent which will decrease the viscosity, or the force tending to separate the two liquids of the emulsion may be greatly increased by the use of the centrifuge. The centrifuge has been successfully used recently in separating water from water-tar emulsions which were formerly dumped untreated into streams.

Salts which are soluble in water are sometimes used in rather high concentrations (5 to 10 percent) to "salt out" an oil-in-water emulsion. The action of the salt is probably to decrease the solubility of the emulsifying agent in water.

The electrical breaking of some of the troublesome emulsions formed in the pumping of crude petroleum is based upon the fact that an electric charge decreases the surface tension of a liquid and electrolizes stabilizing salts. In the emulsions in question, water is dispersed in the oil, so the electrical conductivity is very low. The high voltage alternating current acts on the water globules as though they were plates in an electrical condenser and the oil the dielectric, alternately charging and discharging their surface. The result is to destroy the stabilizing film by causing rapid changes in the surface tension, whereupon the water separates out. These emulsions were formerly burned or thrown out to find their way into natural drainage channels.

SUMMARY.

The term colloid is applied to any substance which on account of its degree of subdivision or dispersion and partial solubility exhibits properties intermediate between those of true solutions and mechanical, unstable suspensions. A division into the following two groups is useful—one in which the solution link is a part of the particle (endo-link) and a second in which another substance, usually an emulsoid colloid, is added to form an exo- or double-solution-link.

The endo-link sols may further be divided into two classes as follows: (a) *Suspensoids*. The disperse phase particles in this class are solids (in some cases sols, containing small liquid globules made rigid by their surface tension, should be included) with a relatively weak solution link. These sols are characteristically of low concentration and low viscosity, are not easily produced, are electrolytes, are easily coagulated by low concentration of other electrolytes and occasionally may be studied with the ultramicroscope if particles are large. (b) *Emulsoids*. The dispersed phase has a stronger tendency to combine with the continuous phase. These sols are easily obtained in high concentration with a high viscosity and are not easily precipitated by low concentrations of electrolytes. In higher concentrations electrolytes affect the equilibrium between the disperse and continuous phase, increasing or decreasing the degree of dispersion according to the direction of this effect. A large number of examples are of bio-

logical origin. Emulsoid particles may be ionically charged, but the charge is a less important property of the sol than it is in the case of suspensoids; their specific gravities and refractive indices are not far from those of the continuous phase. Since many of these sols are ampholytes they are particularly sensitive to changes of hydrogen-ion concentration. Viscosity has been extensively used in the study of these sols as a means of observing the process of gelation or the reverse process, peptization or dispersion.

The exo-link sols are characterized as mentioned above by the presence of a stabilizing agent. In the majority of cases this stabilizer is itself a colloid of the emulsoid class and owes its stabilizing effect to its tendency to combine with the continuous phase. (An exception to this rule is the group of emulsions stabilized by solid particles.) Two classes of these sols are suggested. (c) *Protected Colloids.* These are sols in which solid particles are dispersed in a liquid containing an emulsoid. They are more resistant to the action of salts than suspensoids. (d) *Emulsions.* Members of this class are composed of two immiscible liquids plus an emulsoid colloid soluble in one of them. The liquid in which the stabilizer or link is soluble becomes the external phase. In texture and many physical properties emulsions resemble emulsoids. To prepare or to destroy an emulsion, a knowledge of the character of the emulsifying agent is essential. Where this is impossible other means of attack have been suggested.

Chapter III.

Composition, Properties and Occurrence of Water.

Water is so commonly and so generally used as a solvent for carrying out chemical reactions in which it apparently undergoes no change itself that there is a tendency to regard it as an homogeneous inert substance. This tendency needs only to be pointed out to be corrected. A little consideration of a few very common facts convinces us that in the first place water is neither physically nor chemically homogeneous. Even the purest water has certain properties which force us to consider it as a mixture and in some cases not a very simple mixture.

Before taking up the more complex question of naturally occurring waters and their reactions, it will be necessary to consider the composition and some of the important physical and chemical properties of pure water, as nearly pure, at least, as chemists can prepare it.

Molecular Structure of Liquids.

In physical chemistry two kinds or classes of liquids are recognized. Those which appear to have a uniform molecular weight, usually the same as the vapor, between their freezing and boiling points are called non-associated. The liquid hydro-carbons and many of their derivatives belong to this class. These liquids are apparently homogeneous and their density, viscosity and various other physical properties vary directly as would be expected when subjected to changes of temperature and pressure. They are sometimes called normal liquids. There may be objections to this designation but it is certain that their behavior is less complicated than the other class.

The second class of liquids includes those whose properties indicate that they are made up of two or more molecular polymers. They are called associated liquids because two or more simple molecules are "associated" to form the complex molecules of which the liquid is composed. These liquids show points of inflection in their temperature-density curves, do not show the expected reactions to pressure, and have a number of other characteristics which will be described later. The class includes water, some of the alcohols, liquid ammonia and

various other liquids. (For a more complete list of associated and non-associated liquids, works on physical and inorganic chemistry should be consulted.)

Intra-molecular Structure of Water.

Water is chemically composed of two atoms of hydrogen and one of oxygen so combined that the two hydrogen electrons with six oxygen electrons form a tetrahedron [1] (*see* Fig. 4). To follow the structure still deeper we may say that water is composed of three positive nuclei and ten electrons, one of the positive nuclei and two of the electrons forming the kernel of the oxygen atom, the remaining eight electrons arranged in four pairs to form a tetrahedron and the remaining two positive nuclei held by two pairs of electrons, probably the whole in motion like a minute solar system. It will be well to bear this formula in mind since it helps to explain several important properties of water referred to later.

Molecular Composition of Water.

Physically water is usually considered as existing in three states, the solid, the liquid, and the gaseous, or ice, water and steam or vapor. It appears, however, that the liquid phase is not simple and homogeneous but is composed at ordinary temperatures principally of associated molecules $(H_2O)_2$, $(H_2O)_3$ and probably $(H_2O)_4$, etc. At 4° C., the temperature of greatest density, water is probably largely $(H_2O)_3$. Warming decomposes these aggregates so that water vapor at the boiling point is about 90 percent H_2O. At a moderate temperature then, pure water would contain $(H_2O)_3$, $(H_2O)_2$, H_2O, H^+, and OH^-. At 20° C. it is estimated that water contains 33 percent $(H_2O)_3$ and very little H_2O; at 100° C. one percent $(H_2O)_3$ is still supposed to be present.

Latimer and Rodebush [2] in an extension of the Lewis theory of valence have made a plausible suggestion as to the way in which these molecular aggregates may be built up. They cite several instances in which a hydrogen nucleus acts as a valence bond by sharing two pairs of electrons with two different atoms. Their suggestion would be to consider dihydrol as formed thus: H:$\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}$:H:$\dot{\underset{\cdot\cdot}{\underset{\cdot\cdot}{O}}}$:H and trihydrol

H

[1] Lewis, G. N., Am. Chem. Soc. Monograph, *Valence and the Structure of Atoms and Molecules*, p. 82.

[2] *J. Am. Chem. Soc.* **42**, 1419 (1920).

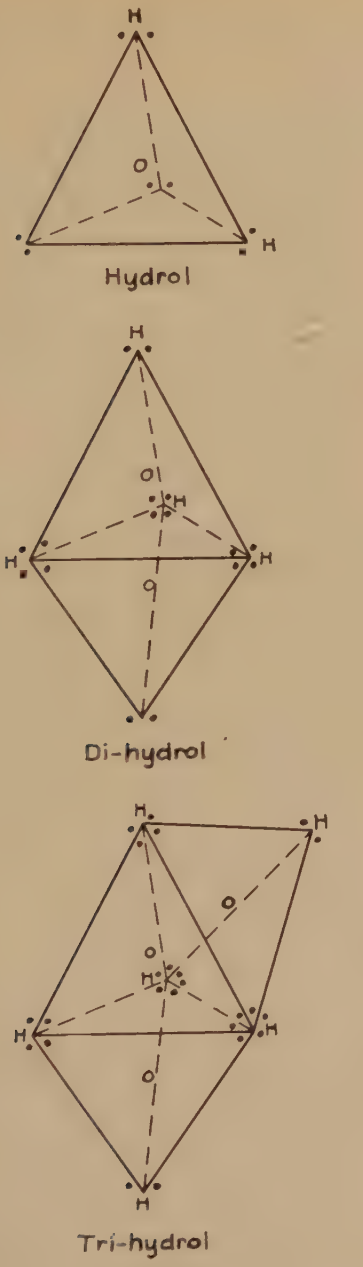


FIG. 4.—Suggested Structure of Water Molecules.

$H:\ddot{O}:H:\ddot{O}:H:\ddot{O}:H$, or, if we consider the four electron pairs of the oxygen shell disposed toward the corners of a tetrahedron, it would appear that a double or triple "hydrogen bond" might exist as is suggested in Figure 4. There is no reason to suppose that the association is limited to groups of two or three. In fact one can easily imagine the possibility of long twisted chains. It is to be hoped that this theory of the constitution of water will be subjected to experimental investigation.

Leaving out the ionization for the present we see that we must have the various molecular forms in equilibrium thus:

$$2(H_2O)_3 \rightleftarrows 3(H_2O)_2 \rightleftarrows 6H_2O \qquad (1)$$

Physical Properties of Water.

Most of the so-called anomalous physical properties of water are to be explained in the light of these equilibria (1). For example, the change of density with temperature passes through a maximum at 4° C. and 1 atmosphere pressure. This is due to the fact that increase of temperature displaces the equilibrium to the left and that the density of $(H_2O)_2$ is less than that of $(H_2O)_3$. From 0° to 4° the increased formation of $(H_2O)_3$ more than offsets the normal expansion with heat. Above 4° the expansion with heat is the predominating effect. The very high specific heat of water (higher than any other liquid except liquid ammonia) is due to the heat absorbed by disassociation.

The effect of pressure is to displace the equilibrium toward the formation of $(H_2O)_3$, hence it lowers the temperature of the point of maximum density and of the freezing point. For the same reason the effect of pressure at temperatures up to 35° C. is to decrease rather than increase the viscosity. Solutes in general also displace the equilibrium to the right. The addition of salts therefore decreases the compressibility. The lowering effect of salts on the specific heat of water is to be explained in the same way. The effect of temperature on the optical properties, refractive, index, etc., also furnishes evidence of the "association" of water molecules.

Water has several other interesting physical properties. Its surface tension is the highest of any liquid except mercury, and it has a high specific gravity. Its boiling point is high when compared with other substances of similar chemical compositions. From anology with

TABLE 2.—*Absorption Spectra of Water.*[1]

λ	8,490	8,430	8,380	8,280	8,220	8,160	8,130	8,065
a	724	755	693	766	713	787	766	787
λ	7,940	7,880	7,830	7,700	7,650	7,545	7,490	7,440
a	693	777	766	787	766	810	799	810
λ	7,410	7,275	7,110	6,955	6,920	6,765	6,730	6,090
a	787	844	821	832	821	879	867	2,526
λ	5,470	5,420	5,270	4,700	3,930	3,020	2,147	1,956
a	335	342	308	545	204	2,733	27.8	123.2
λ	1,708	1,500	1,281	1,243	1,095	990-1,002	800	.....
a	11.4	38.4	1,171	1,221	0.188	0.416	0.0204	.....
λ	750-775	737	725	712	700	687	675	.....
a	0.0241	0.02210	0.00390	0.0084	0.00553	0.00371	0.00329	.....
λ	662	650	637	625	612	600	587	.....
a	0.00020	0.00255	0.00229	0.00223	0.00192	0.00163	0.00051	.....
λ	575	562	550	537	525	506	500	.....
a	0.00020	0.00030	0.00036	0.00005	0.00015	0.00025	0.00025	.....
λ	475	450	300	260	240	230	220	.....
a	0.00020	0.00020	0.00151	0.00254	0.00316	0.00338	0.00567	.....
λ	210	200	193	186	.....	.....	.....	.....
a	0.00610	0.00899	0.01653	0.06884	.....	.....	.....	.....

[1] Kayser, *Absorption Spectrum of Water*, pp. 389-399.

similar chemical substances we would expect it to boil at $-120°$ instead of $+100°$ C.

The absorption of radiant energy ("light") by water is of considerable importance since it has a bearing on the color of water and also on the efficiency of one method of water treatment. Table 2 gives the absolute coefficient (a) figured from $I = I_o e^{-ad}$ (d in cm.) for water from 186 μμ to 8.49 μ (8490 μμ) as shown in Table 2. λ is the wave length in μμ.

From these data it appears that there is very little absorption in the visible, somewhat more in the ultra violet and that water is almost opaque in the infra red.

Absorption in the red accounts for the blue color of large bodies of water. This blue color is composed of (a) light reflected from the surface which is white and polarized, and (b) light reflected from small particles floating in the water and from the bottom, if the depth is not too great. The light reflected from objects below the surface has its red and yellow intensity decreased in proportion to the length of its path through the water. The more turbid the water the shorter is the path and hence the less blue the color. However, the reflecting surfaces (particles of turbidity or the bottom) may themselves have a color or a selective action on the light. In this case the color of the water will be affected accordingly. Colored dissolved substances have an obvious effect. Dissolved colorless salts have no effect. The color and intensity of the light reflected from the surface of the water depends upon the condition of the sky, and the apparent color will therefore depend upon the combination of all of these factors, namely, the quality of incident light (condition of the sky), the amount of turbidity or depth of bottom, and the color of the suspended particles and of the bottom.

The diffusion coefficient of water vapor into air is 0.193.[3] The rate of evaporation is limited by diffusion, which is the slowest step in the process, and therefore evaporation takes place most rapidly at the edges of the lake or reservoir. Evaporation does not take place in direct proportion to the area of the exposed surface but at a considerably slower rate. In absolutely still circular areas evaporation takes place about in proportion to the square root of the area.

The compressibility at 0° is 0.00005 per atmosphere. The compressibility decreases as the temperature or pressure is increased. It

[3] Mellor, Comprehensive Treatise, Inorganic & Theoretical Chem., pp. 339 and 469.

also decreases with the addition of soluble salts, sea water having about 92 percent of the compressibility of pure water.

The vapor pressure of water is a function of temperature under ordinary conditions, amounting to 4.5 mm. of mercury at 0°, 9.1 mm. at 10°, 17.4 mm. at 20°, and 760 mm. at 100° C. It has been shown both mathematically and experimentally, however, that the vapor pressure is less for a concave surface and greater for a convex surface. The increased vapor pressure for convex surfaces becomes appreciable only when the radius of curvature is very small, in the neighborhood of one-millionth of centimeter or 10 μμ. The effect would therefore be noticeable only in a mist or very fine spray.

The surface tension of water, as has been mentioned, is higher than that of most liquids. The actual values for water and some other liquids are as follows (figures are dynes per cm.): mercury — 547 water — 75.0, liquid ammonia — 29.2, benzene — 29.2, alcohol — 22, ether — 16.5.

Water is a poor conductor of heat as compared with most solids but not as compared with other liquids.

The electrical conductivity of pure water is very low, and dry ice is said to be one of the best insulators. The resistance of 1 mm. of pure water at 0° C. is equivalent to 40 million kilometers of copper wire of a similar cross-section, or more than enough to reach 1000 times around the earth at the equator. The dielectric constant of water, 81.7, is relatively high as compared with 34 for methanol, 26 for ethyl alcohol and 2.3 for benzene.

Ice. The freezing point of water (0° C. at 1 atmosphere pressure) is lowered by 0.0075° per atmosphere. Clear, quiet water protected from dust may be supercooled 12° to 15° C. Water crystallizes in prisms or plates of the hexagonal system but individual crystals are rarely found. Four other forms of ice are known but they are formed at relatively enormous pressures and are of theoretical interest only. They are heavier than water. Anchor ice is formed under conditions such that crystallization starts from the bottom—for example, in a shallow rapidly flowing stream where the current prevents the formation of ice on the surface. It has the same density as ice formed at the surface. Pure ice is clear and of a bluish color. Artificial ice may be milky due to fine bubbles of air caught by too rapid freezing or precipitation of dissolved salts.

The density of ordinary ice is 0.918 at 0° C. and at absolute zero (— 273° C.) it is 0.9368, the expansion between these two temperatures being about 10 percent.

Chemical Properties of Water.

Ionization. Probably the most important and extensively studied property of water from a chemical standpoint is its ability to cause the dissociation or ionization of certain substances when dissolved in it. The characteristics of ionization and its relation to chemical reactions in water solution have already been discussed.

A brief survey of some of the suggested explanations of this property may help in understanding the chemistry of water.

The dissociation or ionization of substances in solution is observed in other solvents than water but only when the dielectric constant of the solvent is relatively high. We also find (Nernst-Thompson rule) that the degree of ionization is greater, the higher the dielectric constant. This rule holds for the more strongly polar compounds and would suggest that ionization occurs when a layer of the liquid comes between the positive and negative ions of the molecule and thereby greatly lessens the attractive force and increases the equilibrium distance between them. For instance, the force between Na^+ and Cl^- which exists in the solid is decreased by 99 percent when the salt is dissolved in water which has a dielectric constant of 80.

Brühl[4] before the announcement of Lewis' valence theory called attention to the tetravalent character of oxygen and suggested that the "latent valency" of oxygen explained the hydration of ions and that this in turn at least partially explained the mechanism of ionization. He cited the so-called "anomalous" properties of water, i.e., its volume changes with temperature, etc., and the following facts as bearing on this point: (1) other solvents which cause ionization contain OH groups; (2) substances capable of uniting with water are hygroscopic, and (3) hydrates with water of crystallization are known. This "latent valency" is easily explained from the Lewis formula for water (*see* p. 6). The two free pairs of electrons can combine with ions (e.g., H^+) and form a relatively stable complex. Since the hydrogen ion is never separated very far from a pair of electrons it is not possible to explain the ionization of acids as being brought about by the separation of the hydrogen ion from the acid radical by a dielectric medium, and in fact the ionization of acids does not follow the Nernst-Thompson rule. If, however, the molecules of the solvent can take on hydrogen ions as shown above to form complexes, then ionization may occur.

[4] Brühl, J. W., *Ber.* **28,** 2866 (1895).

Stability. An outstanding characteristic of water is its stability. It may be decomposed into its elements by an electric current, and hydrogen may be displaced by reaction with metals, but water is only slightly decomposed at temperatures of 2000° to 3000° C. and is only slightly affected by other conditions which would decompose it into hydrogen and oxygen.

It must not be assumed, however, that water is chemically inert; quite the contrary. In fact, to merely list all the chemical reactions of water would take more space than is here available. We shall necessarily limit ourselves to those reactions which are of practical importance in water works practice.

Chemical Activity. When water reacts with certain metals liberating hydrogen it may be regarded as an *acid*. In this reaction the metal is oxidized, hence water is an *oxidizing agent*

$$4H_2O + 3Fe \rightleftarrows Fe_3O_4 + 4H_2.$$

Fortunately this particular reaction does not take place at ordinary temperatures or corrosion troubles would be worse than they are.

In hydrolysis, which is discussed elsewhere, water may be considered as both an *acid* and a *base,* e.g.,

$$\text{I.} \quad \begin{aligned} NaHCO_3 + HOH &\rightleftarrows NaOH + H_2CO_3 \\ NaHCO_3 + HCl &\rightleftarrows NaCl + H_2CO_3 \end{aligned}$$

$$\text{II.} \quad \begin{aligned} AlCl_3 + 3HOH &\rightleftarrows Al(OH)_3 + 3HCl \\ AlCl_3 + 3NaOH &\rightleftarrows Al(OH)_3 + 3NaCl \end{aligned}$$

In its reactions with the halogens water is a *reducing agent,* for the free halogen is reduced and oxygen is formed.

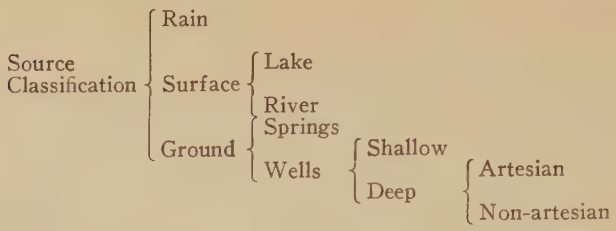
$$2H_2O + 2Cl_2 \rightleftarrows 2HCl + 2HClO \rightleftarrows 4HCl + O_2.$$

So we see that water can be an *acid,* a *base,* an *oxidizing* agent, or a *reducing* agent. Rather than inert we must consider it as a very active chemical reagent.

Finally, water has been referred to as the solvent par excellence. A wide range of substances are appreciably soluble in water, some are soluble in the presence of other solutes and still others form relatively permanent colloidal sols so that they must be reckoned with in considering the composition of natural waters.

Occurrence of Water.

The classification of waters as to source is rather obvious and the following scheme needs little explanation.



It should be noted that the source of the water determines the kind and amounts of dissolved substances which it carries. Rain water will naturally carry the least, surface water considerably more and ground water the most matter in solution. Exception can of course be taken to this as to any broad generalization. For instance a stream fed by melting mountain snow may near its source contain less in solution than rain collected in a city, and well or spring water in a region of igneous rock formations does not hold as much dissolved matter as an ordinary stream in a sedimentary region.

Lake water may be expected to be less turbid than river water in the same region because of the opportunity for sedimentation. While lakes and rivers are ordinarily referred to as surface waters cases may arise where they are spring-fed to such an extent that they may be considered as ground waters.

The terms "spring" and "well" are used in their usual sense. The meaning of the adjectives "deep" and "shallow" depends too often on local usage and for that reason the classification is of doubtful value. A "shallow" well is usually one which does not penetrate an impervious stratum, is frequently dug rather than drilled, and is fed by seepage from the surrounding soil. Such wells are more subject to pollution, frequently become turbid after a rain, and are likely to dry up during a drought. "Deep" wells penetrate to some water-bearing stratum usually lying beneath an impervious stratum. Such wells, if properly cased, are not easily affected by surface pollution and are usually independent of wet or dry weather. If the water-bearing stratum is sufficiently extensive it will serve as a reservoir to supply the well even during prolonged drought. Artesian wells are those in which the water is under pressure so that it rises above the stratum from which it comes but *not necessarily above* or even up to the ground level. The term "flowing well" has so many colloquial shades of meaning that we shall avoid its use.

Chapter IV.

Chemical Composition of Natural Waters.

Since practically all known substances are soluble to at least a slight extent in water, a wide variation in the chemical composition of natural waters is to be expected. Table 3 is a list of substances which have been observed in water.

TABLE 3.— *Substances Occurring in Water.**

I. Common ingredients:
- Acids: carbonic, sulfuric, hydrochloric, silicic, etc., usually in combination.
- Aluminium: oxide and sulfate.
- Calcium: carbonate, chloride, sulfate, phosphate.
- Iron: carbonate, bicarbonate, oxide, sulfate.
- Lithium: carbonate, bicarbonate, sulfate, chloride.
- Magnesium: sulfate, carbonate, bicarbonate, chloride.
- Potassium: carbonate, bicarbonate, chloride, sulfate, and phosphate.
- Silicon: usually as silica or silicon dioxide; occasionally as the bicarbonate.
- Sodium: chloride, carbonate, bicarbonate, sulfate.

II. Rarer ingredients:
- Acids: crenic and apocrenic, usually as crenates.
- Ammonium: nitrate, chloride, crenate.
- Antimony: as oxide and sulfate.
- Arsenic: arsenate of sodium and potassium; arsenous acid.
- Barium: as baryta or barium oxide and the sulfate.
- Boron: as biborate of soda or borax.
- Bromine: as bromides of sodium, potassium, etc.
- Cadmium: as sulfate (very rare).
- Caesium: as sulfate (very rare).
- Chlorine: as chlorides; rarely free.
- Cobalt: very rare.
- Copper: very rare.
- Fluorine: as fluorides in two or three springs.
- Iodine: as iodides of sodium and potassium.
- Lead: very seldom seen.
- Rubidium: very rare.
- Strontium: very rare.
- Zinc: very rare.

* Crook, *Mineral Waters of the United States.* Lea Bros., 1899.

Besides the above-mentioned solids the following gases are commonly found in mineral springs:

Carbonic anhydride, or carbonic-acid gas.
Hydrogen sulfide, or sulfuretted hydrogen gas.
Oxygen.
Nitrogen.
Carbureted hydrogen: very rare.

With so large a variety of substances found in waters it is natural that several classifications should be proposed. These different systems have been discussed and compared by Crook,[1] Haywood[2] and Bartow.[3] Haywood's modification of Peale's classification seems to be the most useful and is therefore given (Table 4).

TABLE 4.—*Classification of Chemicals Found in Water.**

Class	Subclass	Groups: Thermal	Groups: Non-thermal
I. Alkaline	Carbonated or bicarbonated	Sodic	
	Borated	Lithic	
	Silicated	Potassic	
		Calcic	Nongaseous
		Magnesic	Carbondioxated
II. Alkaline-Saline..	Sulfated	Ferruginous	Sulfuretted
	Muriated	Aluminic	Azotized
	Nitrated	Arsenic	Carbureted
		Bromic	Oxygenated
		Iodic	
III. Saline	Sulfated	Silicious	
	Muriated	Boric	
	Nitrated		
IV. Acid	Sulfated		
	Muriated		

* Haywood, *U. S. Dept. Agric. Bur. Chem. Bull.* 91.

The classification of Haywood & Peale given above was designed primarily for use in distinguishing different types of saline waters and really has little significance when applied to waters of low mineral content. The concentrations of saline waters reach very high figures; perhaps the highest are those for the Dead Sea which is said by Raich[4] to have a salt content of over 22 percent. These saline waters are of interest principally from a therapeutic standpoint and really require treatment in a separate volume.

Bartow points out that these classifications are all of limited value since they refer to the *kinds* with no reference to the *amounts* of constituents. Two waters which carried the same substance in solution

[1] *Mineral Waters of the United States*, 1899.
[2] *U. S. Dept. Agric. Bur. Chem. Bull.* 91.
[3] *Ill. State Water Survey Bull.* 4.
[4] *Chem. Ztg.* 31, 845.

would be classed the same although the one might contain 200 and the other 20,000 parts per million of total dissolved matter.

Units for Reporting Water Analyses.

The standard unit in this country is one part per million (ppm.) which for most ordinary cases is the same as milligrams per liter within the limits of analytical error. Some laboratories report in grains per gallon (gr./gal.) as well as parts per million. Since there are 58,300 grains in a U. S. gallon the factor parts per million to grains per gallon is 0.0583. The imperial gallon contains 70,000 grains and is used to some extent as a unit in Great Britain. Occasionally an analysis reported in parts per hundred thousand is seen in this country; it is apparently standard in England. There is also the French degree for reporting hardness which is parts per 100,000 of calcium carbonate or equivalents, and the German degree which is parts per 100,000 of calcium oxide or its equivalents.

Classification of Waters According to Amount of Dissolved Constituents.

The characterization of a water as "hard" or "soft," or "saline" or "non-saline" is so much a question of what one is accustomed to that to attempt a general classification is hazardous.

Since in waters of low total solid residue the principal constituents found are those which produce hardness, we shall not distinguish between hardness and total solids in the following classification.

Class	Total Solids
Soft	Less than 100 ppm.
Moderately hard	100-200 ppm.
Hard	200-500 ppm.
Saline	500 ppm. and over

Such arbitrary limits are bound to be subject to criticism. The limit of 100 ppm. for soft water is chosen because it is just about the point where the water softener salesman begins to have difficulty in demonstrating the advantages of his treatment. Up to 200 ppm. the hardness of the water is not seriously complained of. Above 200 ppm. the mineral constituents of the water are a serious drawback for both domestic and industrial use. Above 500 ppm. the water has a salty or brackish taste detectable by most people and a cathartic effect is usually observable by persons not accustomed to so highly mineralized a water. The writer has known of the use of water

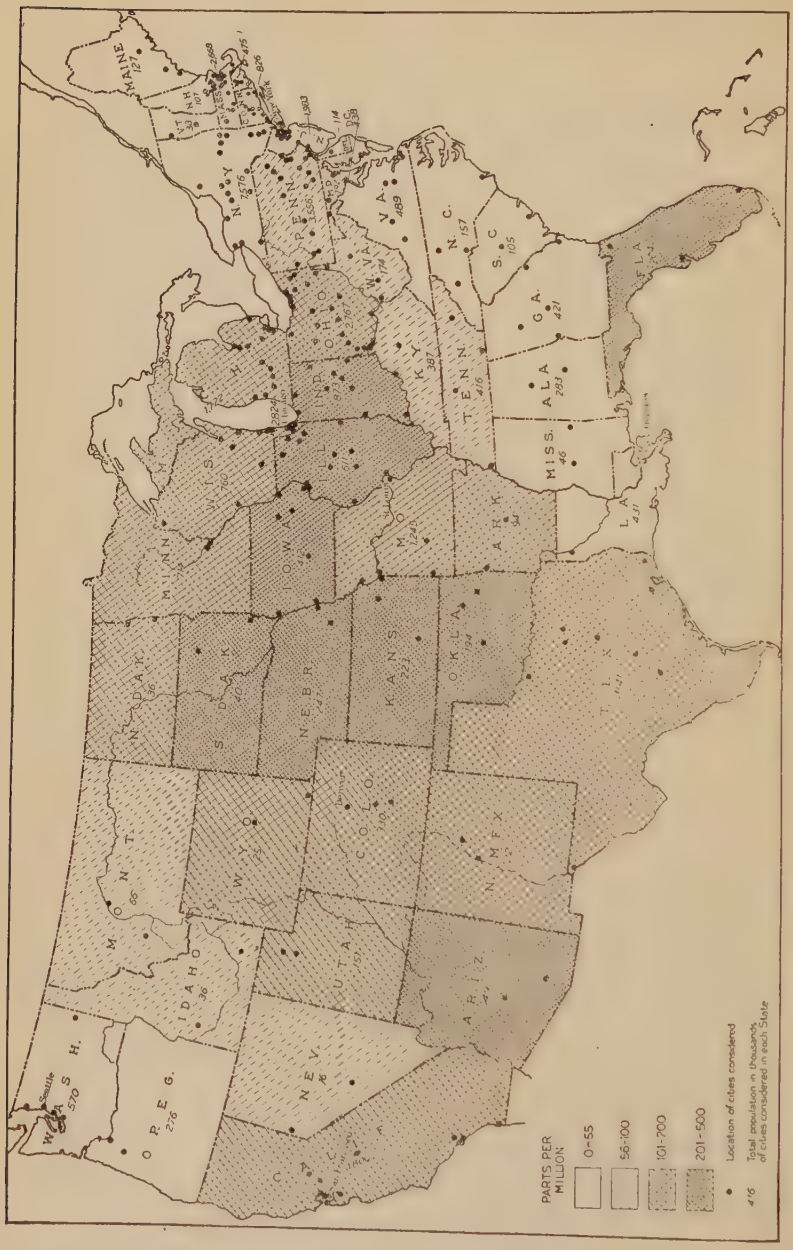


FIG. 5.—Average Hardness, by States, of Water Furnished by Public Supply Systems in the United States (from U.S.G.S. Water Supply Paper 496).

containing 2000 ppm. total residue as a public supply. The average hardness by States in the United States is shown in Figure 5.[5]

Substances Commonly Found in Natural Waters.

The substances more commonly met with in natural waters and those which must be considered in water treatment are shown in the following figure (Fig. 6), originally prepared by the author for the

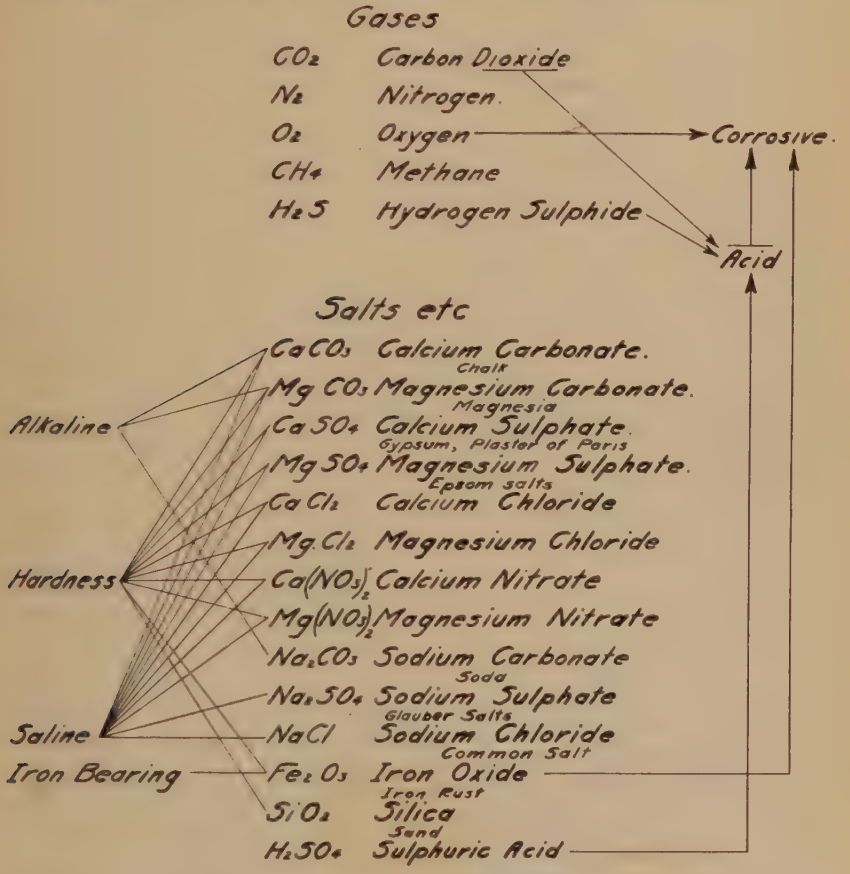


FIG. 6.—Substances in Natural Waters.

publication on "Water Works Practice" of the American Water Works Association. It must be noted that this figure does not purport to be an analysis of an actual water but merely a list of the substances commonly or occasionally found. Sulfuric acid could not exist with

[5] U. S. Geological Survey, *Water Supply Paper No. 496*, by W. D. Collins.

calcium carbonate nor would sodium carbonate occur in a water containing calcium sulfate.

The combinations of substances commonly found have been classified by Bartow as follows:

Class I includes those waters which contain more than enough sodium to unite with all of the nitrate, chloride and sulfate ions.

Examples, Class I

Determinations Made by Analysis		Hypothetical Combinations		
	Parts per Million		Parts per Million	Grains per Gallon
Iron (Fe)	1.2	Potassium Nitrate (KNO_3)	2.3	.13
Manganese (Mn)	0.0	Potassium Chloride (KCl)	6.1	.36
Silica (SiO_2)	14.1	Sodium Chloride (NaCl)	1.8	.11
Nonvolatile	1.8	Sodium Sulfate (Na_2SO_4)	1.7	.10
Alumina (Al_2O_3)	0.0	Sodium Carbonate (Na_2CO_3)	77.3	4.52
Calcium (Ca)	66.9	Ammonium Carbonate ($(NH_4)_2CO_3$)	14.3	.83
Magnesium (Mg)	31.4	Magnesium Carbonate ($MgCO_3$)	108.7	6.34
Ammonia (NH_4)	5.3	Calcium Carbonate ($CaCO_3$)	167.0	9.75
Sodium (Na)	34.8	Iron Oxide (Fe_2O_3)	1.7	.10
Potassium (K)	4.1	Silica (SiO_2)	14.1	.82
Sulfate (SO_4)	1.2	Nonvolatile	1.8	.11
Nitrate (NO_3)	1.4			
Chloride (Cl)	4.0	Total	396.8	23.17
Alkalinity				
Phenolphthalein	0.			
Methyl Orange	376.			
Residue	380.			

Determinations Made by Analysis		Hypothetical Combinations		
	Parts per Million		Parts per Million	Grains per Gallon
Iron (Fe)	1.0	Potassium Nitrate (KNO_3)	49.0	2.86
Manganese (Mn)	0.0	Potassium Chloride (KCl)	127.9	7.47
Silica (SiO_2)	15.2	Sodium Chloride (NaCl)	2083.8	121.69
Nonvolatile	0.5	Sodium Sulfate (Na_2SO_4)	119.7	6.99
Alumina (Al_2O_3)	1.8	Sodium Carbonate (Na_2CO_3)	250.7	14.64
Calcium (Ca)	29.3	Magnesium Carbonate ($MgCO_3$)	54.8	3.20
Magnesium (Mg)	15.8	Calcium Carbonate ($CaCO_3$)	73.1	4.27
Ammonia (NH_4)	0.0	Iron Oxide (Fe_2O_3)	1.4	0.08
Potassium (K)	86.0	Alumina (Al_2O_3)	1.8	0.10
Sodium (Na)	967.2	Silica (SiO_2)	15.2	0.89
Sulfate (SO_4)	81.0	Nonvolatile	0.5	0.03
Nitrate (NO_3)	30.1			
Chloride (Cl)	1325.0	Total	2777.9	162.22
Alkalinity				
Methyl Orange	362.			
Residue	2792.			

These waters would therefore contain sodium carbonate and possibly the carbonates of magnesium, calcium and iron. The waters of this class will form a sludge or soft scale when used in boilers.

Class II includes those waters which have sufficient sodium to unite with all of the nitrate and chloride and with part of the sulfate ions present. These waters contain the sulfate of magnesium and sometimes the sulfates of calcium, iron and aluminum. The waters of this class will form a scale more or less hard, according to the proportion of sulfate present. Lime and soda are both required for softening.

Examples, Class II

Determinations Made by Analysis		Hypothetical Combinations		
	Parts per Million		Parts per Million	Grains per Gallon
Iron (Fe)	0.8	Potassium Nitrate (KNO_3)	2.8	.16
Manganese (Mn)	0.0	Potassium Chloride (KCl)	7.3	.43
Silica (SiO_2)	8.9	Sodium Chloride (NaCl)	19.0	1.11
Nonvolatile	3.6	Sodium Sulfate (Na_2SO_4)	27.8	1.62
Alumina (Al_2O_3)	2.3	Ammonium Sulfate ($(NH_4)_2SO_4$)	2.2	.13
Calcium (Ca)	174.2	Magnesium Sulfate ($MgSO_4$)	306.8	17.90
Magnesium (Mg)	62.1	Calcium Sulfate ($CaSO_4$)	37.4	2.18
Ammonia (NH_4)	0.6	Calcium Carbonate ($CaCO_3$)	407.2	23.79
Sodium (Na)	16.4	Iron Oxide (Fe_2O_3)	1.1	.06
Potassium (K)	4.9	Alumina (Al_2O_3)	2.3	.13
Sulfate (SO_4)	292.0	Silica (SiO_2)	8.9	.52
Nitrate (NO_3)	1.8	Nonvolatile	3.6	.21
Chloride (Cl)	15.0	Total	826.4	48.24
Alkalinity Methyl Orange	394.0			
Residue	812.0			

Class III includes those waters in which the sodium is not present in sufficient quantity to unite with all of the nitrates and chlorides present. These waters will therefore contain magnesium chloride. The hardness may be due to chlorides, sulfates and carbonates of magnesium, calcium, etc. These waters will be corrosive and will form a hard scale when used in boilers.

The common notion that wells and springs maintain a constant chemical composition is apparently unfounded. Haywood[6] reports a decrease of 50 percent in the mineral content of certain springs from 1871 to 1905, while the author has observed an increase of 100 percent in the solids of certain wells in a period of 20 years.

[6] *Loc. cit.*

Examples, Class III

Determinations Made by Analysis		Hypothetical Combinations		
	Parts per Million		Parts per Million	Grains per Gallon
Iron (Fe)	0.7	Potassium Chloride (KCl)	27.6	1.61
Manganese (Mn)	0.0	Sodium Chloride (NaCl)	904.2	52.80
Silica (SiO_2)	32.8	Ammonium Chloride (NH_4Cl)	6.9	0.40
Nonvolatile	8.0	Magnesium Chloride ($MgCl_2$)	139.1	8.12
Alumina (Al_2O_3)	2.6	Magnesium Sulfate ($MgSO_4$)	141.6	8.27
Calcium (Ca)	112.3	Calcium Sulfate ($CaSO_4$)	180.6	10.55
Magnesium (Mg)	64.2	Calcium Carbonate ($CaCO_3$)	200.5	11.71
Ammonia (NH_4)	2.3	Iron Oxide (Fe_2O_3)	1.0	0.06
Sodium (Na)	355.8	Silica (SiO_2)	32.8	1.91
Potassium (K)	14.4	Nonvolatile	8.0	0.47
Sulfate (SO_4)	189.7	Alumina (Al_2O_3)	2.6	0.15
Nitrate (NO_3)	0.0			
Chloride (Cl)	670.0	Total	1644.9	96.05
Alkalinity Methyl Orange	250.			
Residue	1660.			

Determinations Made by Analysis		Hypothetical Combinations		
	Parts per Million		Parts per Million	Grains per Gallon
Iron (Fe)	1.4	Sodium Nitrate ($NaNO_3$)	19.4	1.13
Silica (SiO_2)	12.5	Sodium Chloride (NaCl)	17.2	1.00
Nonvolatile	0.5	Ammonium Chloride (NH_4Cl)	0.9	.06
Alumina (Al_2O_3)	0.9	Magnesium Chloride ($MgCl_2$)	5.2	.31
Calcium (Ca)	77.7	Magnesium Sulfate ($MgSO_4$)	44.7	2.62
Magnesium (Mg)	42.7	Magnesium Carbonate ($MgCO_3$)	11.8	6.54
Ammonia (NH_4)	0.3	Calcium Carbonate ($CaCO_3$)	194.0	11.35
Sodium (Na)	12.0	Iron Oxide (Fe_2O_3)	2.0	.12
Potassium (K)		Alumina (Al_2O_3)	0.9	.05
Sulfate (SO_4)	35.7	Silica (SiO_2)	12.5	.73
Nitrate (NO_3)	14.1	Nonvolatile	0.5	.03
Chloride (Cl)	15.0			
Alkalinity Methyl Orange	318.	Total	409.3	23.94
Residue	405.			

Mineral Waters.

The mineral water industry was originally confined to the bottling and sale of medicinal waters. With the advance of science some of the claims made for these waters were found to be unwarranted. It was found to be necessary to drink several hundred gallons of some so-called Lithia waters in order to obtain a therapeutic dose. With

respect to radioactivity Skinner & Sale [7] state that—"Of all waters, foreign and domestic, which have been analyzed, and from published data it may be concluded that shippers are not justified in making statements on labels which would induce prospective consumers to purchase the waters because of their radioactivity. The largest radioactivity of a temporary nature was found in a water from a warm spring in Massachusetts. Permanent radioactivity was found in greatest measure in a deep well in Northern Ohio. To obtain a daily dose (2 micrograms) prescribed by the American Medical Association as a minimum, the patient would have to consume 2810 gallons of the warm spring water or 1957 gallons for the Ohio well."

The decline in production of medicinal waters has been largely offset by the production of table waters. Reviewing the mineral water industry from 1883 to 1923 Collins [8] reports that it rose from one million dollars in 1883 to eight and a half million in 1903, dropped to four and a half million in 1918 from which it has risen to six and a half million dollars in 1923. In 1923 the medicinal water sales amounted to only 13 percent of the total.

pH of Natural Waters.

Since most natural waters are buffered with calcium bicarbonate and carbonic acid we find their pH ranging from about 7 to 8. In soft waters the organic acids from vegetable decomposition may reduce the pH to 5 or even below, while photosynthetic action (p. 155) in relatively hard waters may raise it considerably above 8. The discharge of trade wastes, mine waters and so forth may produce conditions entirely abnormal.

Composition of Rain Water.

Considerable data on the composition of rain water has been obtained by various agricultural stations. Some data by Woehlk [9] show rather surprisingly large amounts of nitrogen and sulfur. The amounts of nitrogen compounds, chlorine and sulfates in the rains and snows at Mt. Vernon, Iowa, from Oct. 1, 1922 to June 1, 1923, were determined. The town has a population of 2500 without manufacturing enterprises, a condition which eliminates excessive smoke contamination of the atmosphere. Samples were collected in granite pans and

[7] *J. Ind. Eng. Chem.* **14**, 948 (1922).
[8] U. S. Geological Survey, *Mineral Resources of the United States*, 1923, II, p. 109.
[9] *Chem. News* **127**, 3; *Chem. Abstracts* **17**, 3558.

every precaution was used to avoid contamination. In the period 70 inches of snow and 11.2 inches of rain fell, equivalent to 17.21 inches of rainfall. From analyses of samples of 12 snows and 29 rains it was calculated that 2.035 kg. of chlorine, 0.57 kg. of sulfur as SO_3 and 3.93 kg. of nitrogen fell on each acre. In parts per million the chlorine varied from 0.345 to 2.81; nitrogen averaged 0.896 parts per million and was quite constant. Electrical storms seemed to be responsible for some of the higher amounts. The average parts per millon of free ammonia were 0.34, albuminoid ammonia 0.264, nitrogen in nitrates was 0.346, in nitrites 0.397 ppm., and sulfur as SO_3 0.147 ppm. The amount of precipitation determines largely the number of pounds of nitrogen supplied per acre, although slight rains have a higher concentration of nitrogen than long rains. Determinations were made on the basis that one acre-inch of rain weighs 226,875 pounds.

Chapter V.

Economic Disadvantages of Unsuitable Waters.

Soap Waste.

Many of the substances contained in natural waters have chemical properties which are unfavorable to industrial and domestic use of the water. Most of these unfavorable properties are popularly referred to as "hardness." The term as sometimes used is rather indefinite. It is defined in *Standard Methods of Water Analysis* (American Public Health Association, 1923) as follows:

> Water which requires an excessive amount of soap to form a lather or forms much incrustation on vessels in which it stands or is heated is commonly called "hard water." Calcium and magnesium, and iron and aluminium to a less extent, are responsible for these effects. (The pseudohardness of brines is caused by their high sodium content which prevents solution of soda soaps.)

The effect of hard water and the means for water softening appear to have been first discussed by a British chemist by the name of Th. Clark, who patented the lime process in 1841.[1] He later published several papers on the subject of softening by the use of lime and the use of soap solution to determine the hardness of water. They are: "A new process for purifying the water supplied to the metropolis," by Th. Clark, London, 1849; "On the examination of water for towns for its hardness," Th. Clark, *Chem. Gaz.* **5**, 100 (1847); reviewed in detail by J. Moser, *Wien Acad. Ber.* 1850, April, p. 484; abstract *Jahresbericht* **3**, 608.

Soap Waste. The precipitation of soap by calcium and magnesium salts is probably one of the most commonly recognized disadvantages of hard water. The reaction is frequently written (assuming soap to be sodium oleate)

$$2NaCO_2C_{17}H_{33} + CaSO_4 = Ca(CO_2C_{17}H_{33})_2 + Na_2SO_4$$

On the basis of this equation it should require about 0.05 pound of soap to neutralize a hardness of 1 part per million in 1000 gallons of water. The data reported in the literature based on experimental

[1] *Repertory of Patent Inventions for 1841.* (Great Britain.)

determination of soap wasted do not agree with this figure nor is there agreement among the different authorities. The various figures are given in Table 5.

TABLE 5.—*Soap Waste Caused by Hardness of Water.*

Hardness in ppm.	Soap wastes lbs. per thousand gallons per ppm.	Authority
63	0.03	Laundry Owners Nat. Assoc. Manual 1924.
Any	0.05	Calculated from equation.
Any	0.093	Booth, *Water Softening and Treatment.*
Any	0.100	Several water softener mfgrs., also Christie (*Water, Its Purification and Use in the Industries,* p. 14).
76.5	0.070	Robins, Macmillan & Bosart, *Ind. and Eng. Chem.* **18,** 27 (1926).
153	0.070	
236	0.073	
25	0.164	Whipple, *The Value of Pure Water.*
80	0.209	
200	0.192	
10	0.160	Buswell and McRoberts, paper before American Chemical Society, Sept., 1924.
100	0.071	
200	0.065	
300	0.063	

From these data it appears that the reaction does not follow exactly the equation given above. Evidently the precipitated lime soap adsorbs a variable amount of sodium soap, the amount decreasing as the hardness increases so that with waters of 200 ppm. or over the soap destroyed above that calculated from the equation is approximately 25 percent.

Variations in the composition of soap and of the water used in the experiments would account in part for the variations from the equation. The figure 0.1 pound soap wasted per ppm. hardness per 1000 gallons of water appears to agree with laundry experience.

Financial Loss Due to Soap Waste.

A number of interesting figures have been given to emphasize the economic importance of soap waste due to hard water. Such calculations when applied to cities must be based on assumptions as to the amount of water used for washing with soap and the completeness with which the soap reacts with the lime salts, and must be considered as approximations. One gallon per capita per day is usually taken as

the amount of water used for washing. On this basis it was reported [2] that the removal of 72 ppm. of hardness from the water of the city of St. Louis resulted in a saving of $920 worth of soap per day. The writer has estimated that in a town of 40,000 inhabitants using a water of 300 ppm. hardness a ton of soap is wasted per day. It is generally conceded that the saving in soap alone is greater than the cost of municipal water softening. The other benefits of soft water are clear gain. If this is true in the case of cities where all of the water is softened it is clear that for private installations and laundries where it is practicable to limit the softening to that portion of the supply in which it is needed, the saving will be very considerable.

The waste of soap is not the only objection to hard water in laundering. The lime soaps tend to stick to the fabric and are not easily rinsed off. This causes spots and stains on the laundered article.

Boiler Scale.

At least an equally serious effect of hard water is the formation of scale by hard waters when heated. The exact determination of the loss due to scale in steam boilers is rendered difficult by the fact that the water-softening process removes turbidity and corrosive substances along with scale-forming materials so that a comparison of operating costs with and without treatment frequently includes other benefits than prevention of scale alone.

The University of Illinois Engineering Experiment Station Bulletin 11 reports the following losses in fuel efficiency due to the presence of scale in boilers:

TABLE 6.—*Loss in Fuel Efficiency Due to Boiler Scale.**

Character of Scale	Thickness	Composition	Loss of Efficiency
			Per cent
Hard	1/50″	Mostly carbonate	9.4
Soft	1/23″	" "	7.2
Hard	1/32″	" "	8.5
Soft	1/25″	" "	8.0
Hard	1/25″	" sulfate	9.3
Hard	1/20″	" "	11.1
Soft	1/16″	" "	10.8
Soft	1/16″	" carbonate	11.0
Soft	1/16″	" "	12.4
Hard	1/16″	" "	12.6
Soft	1/11″	" "	15.0
Hard	1/8″	" sulfate	15.9

* *Univ. Ill. Eng. Exp. Sta. Bull.* 11.

[2] *Report of Water Commissioner of St. Louis,* 1922.

In summarizing various data Parr [3] states that a conservative estimate would place the loss in fuel efficiency at 10 percent for each 1/16 inch thickness of scale.

The data on the effect of scale on locomotive boilers are more extensive and accessible than those on stationary boilers because of the work of the American Railway Engineers' Association in collecting them. The report of the Water Service Committee of this association for 1925 gives the saving per locomotive per year due to softened water as averaging $1000 for each 10 grains of hardness or $5.88 for each part per million of hardness. Savings in localities where the raw water is very bad have run as high as $8000 per locomotive per year. In 1914 this committee estimated the loss at 7 cents per pound of scale-forming material entering the boiler. This figure was recently revised to 13 cents due to generally increased costs of materials and labor. The 1925 report indicates that the revised figure is too low.

Cause of Scale.

Boiler scale is caused by the precipitation of the less soluble compounds when the water is concentrated in a boiler. These compounds are mainly the salts of calcium and magnesium, or, to be more specific, the sulfate and carbonate of calcium and the oxide or hydroxide of magnesium. The carbonate of magnesium may also be found in scale formed at relatively low temperatures. The oxides of iron and aluminum will be found in the scale if present in the feed water as will the silica. If the feed water is turbid the suspended matter will appear in the sludge or may be included to some extent in the scale. Organic matter either from the feed water or from oil in the condensed steam where a return system is used tends to collect on the inner surface of the boiler and forms a "burnt scale." This scale is a poorer conductor of heat than the lime scale. The amount of scale which will be formed expressed in pounds per thousand gallons of water used may be calculated from the Stabler formula [4]

$$\text{Scale} = 0.00833\ \text{Sm} + 0.00833\ \text{Cm} + 0.0107\ \text{Fe} + 0.0157\ \text{Al} + 0.0138\ \text{Mg} + 0.0246\ \text{Ca}.$$

Where Sm equals the suspended matter, Cm the colloidal matter and the chemical symbols, the amounts of the substances found, all expressed in parts per million. The factors are simply combinations of the stoichiometric factors for converting iron, aluminum and magnesium

[3] *Fuel, Gas, Water and Lubricants*, p. 116.
[4] U. S. Geol. Survey, *Water Supply Paper No. 274*, p. 176.

to the oxides and calcium half to the carbonate and half to the sulfate, and the factor for converting parts per million to pounds per thousand gallons (i.e., 0.00833). (For a more complete discussion of this formula reference should be made to the original article and to *Geological Survey of Ohio*, 4th Series, Bulletin 29, p. 71, Foulk.)

Types and Composition of Scale.

The boiler scales most commonly encountered are of two classes: the *soft* or *carbonate* scales and the *hard* or *sulfate* scales. When a bicarbonate is heated in solution, carbon dioxide is driven off and the carbonate ion formed.

$$2(HCO_3^-) \rightleftarrows CO_3^{--} + H_2O + CO_2$$

Since $CaCO_3$ is only soluble to the extent of 17 to 25 ppm.[5] depending on the completeness with which the carbon dioxide is removed, the formation of a considerable amount of carbonate ion will soon exceed the value for the solubility product constant for calcium carbonate ($[Ca^{++}] \times [CO_3^{--}] = K_{sol}$) and that salt will precipitate. This reaction occurs at relatively low temperature so carbonate scale is most commonly found in feed water heaters and feed lines. As first formed the calcium carbonate is apparently amorphous but eventually crystallizes as calcite. It does not form a hard adherent scale but rather tends to form a sludge. When found as an adherent scale it is in the crystalline form of aragonite.

Hall[6] has called attention to the fact that the solubility of calcium carbonate increases with temperature slightly, so that the point of least solubility in a boiler would be in the body of the liquid and not next to the heated surface. For this reason it tends to form sludge rather than scale. The solubility of calcium sulfate decreases with increase in temperature above 40° C.,[7] so that the point of least solubility is the hottest point next to the heated tube surface. When calcium sulfate separates out it does so in the form of hard adherent scale, crystallized anhydrite. Hall has shown that in a given experiment with a sulfate water 89 percent of the calcium sulfate thrown down in the boiler formed hard scale, while 11 percent was found in the sludge.

Hall's theory points out very clearly why calcium sulfate scale may

[5] Kendal, *Phil. Mag.* (6) **23,** 958; Johnston & Williamson, *J. Am. Chem. Soc.* **38,** 975.

[6] *Ind. Eng. Chem.*, **17,** 283.

[7] Tilden and Shenstone, *Phil. Trans.* **175A,** 31 (1884); Boyer-Guillon, *Am. Cons. Arts Matiere* **3,** 2 (1900); Melcher, *J. Am. Chem. Soc.*, **32,** 50; Hall (*loc. cit.*).

be formed in a boiler when the analysis of the feed water as reported in the usual hypothetical combinations shows no calcium sulfate present. It is because when the concentrations of calcium ion and sulfate ion at the heating surface are such that they exceed the ion solubility product constant for calcium sulfate at that temperature, salt will form. This condition will occur in waters high in any sulfate (Mg^{++}, Na^{+}, etc.), and the ions of calcium carbonate will react with the sulfate forming calcium sulfate and leaving the ions of the corresponding magnesium or sodium carbonate in solution.

Since the carbonate ion is removed to a considerable extent in the feed water heater and in the sludge which is blown down from time to time there is a tendency for an accumulation of sulfates in the boiler. This will naturally result in the formation of more and more sulfate scale as the time between complete washings is prolonged. This is well illustrated by the analyses of scale from two boilers both using the same water, as shown in Table 7.

TABLE 7.—*Composition of Two Boiler Scales.**

	Samples	
	Boiler I	Boiler II
Analysis		
CO_3	5.46	6.86
Ca	24.89	20.04
Mg	5.28	11.60
SO_4	51.04	34.36
SiO_2	2.05	2.56
$Fe_2O_3 + Al_2O_3$	2.14	6.52
Na + K	....	....
$(OH)_2$	7.65	16.54
H_2O	2.03	1.58
Hypothetical Combinations		
$CaCO_3$	9.06	11.38
$CaSO_4$	72.32	48.69
$MgCO_3$	....	2.20
$Mg(OH)_2$	12.63	27.76
$Fe_2O_3 + Al_2O_3$	2.14	6.52
H_2O	2.03	1.58
SiO_2	2.05	2.56

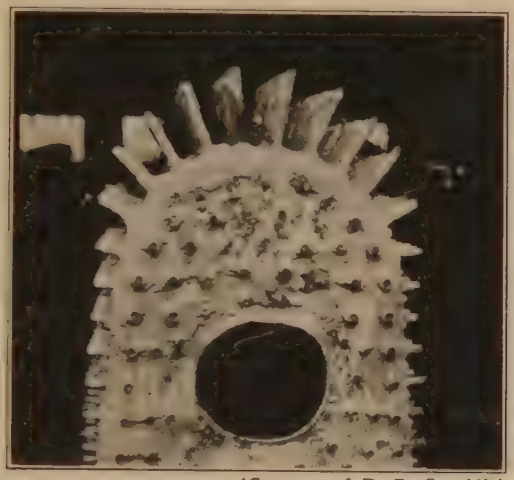
* Bartow and Mohlman, *Ill. State Water Survey Bull.* **11**, 162.

The only difference noted in the operation of these two boilers was that No. I was washed out every four weeks, while No. II was washed out every two weeks. Note the high percentage of calcium sulfate in No. I.

Less frequently encountered are the silicate scales. Hall [8] has

[8] *Loc. cit.*

identified the magnesium silicate $6MgO.3SiO_2.5H_2O$ in some silicate scales. Magnesium carbonate hydrolizes to give magnesium hydroxide which is sometimes an important component in scales. The tables from Hall's paper (Tables 8 and 9) give analyses of typical scales and sludges.



(Courtesy of R. E. Coughlin)

FIG. 7.—Boiler Scale from Hard Water.

TABLE 8.—*Analyses and Classification of Boiler Scales.**

No.	Type of Scale	SiO_2	$Al_2O_3 + Fe_2O_3$	CaO	MgO	Na_2O	SO_3	CO_2	Loss at 105°C.	Net ignition loss
		Percent								
1	Sulfate	1.5	2.2	38.6	1.6	..	54.5	0.0	0.5	1.5
2	Sulfate	3.1	1.2	36.9	5.9	..	45.6	3.3	0.2	4.0
3	Sulfate	0.7	0.4	39.0	2.5	..	55.4	0.0	0.2	1.7
4	Sulfate-carbonate	4.2	1.2	37.5	11.2	..	24.1	15.7	0.4	5.5
5	Carbonate	0.7	1.2	51.1	3.7	..	0.4	42.1	0.1	1.0
6	Carbonate	1.5	1.0	52.9	1.8	..	0.8	40.1	0.1	2.0
7	Carbonate-silicate	17.1	1.8	26.1	22.8	..	0.9	20.2	1.6	9.4
8	Carbonate-silicate	9.7	1.7	29.1	24.2	..	0.8	22.7	1.5	10.1
9	Carbonate-silicate	10.4	1.2	22.1	35.0	..	0.2	17.1	0.5	13.9
10	Carbonate-silicate-sulfate	12.0	1.4	34.1	14.1	..	10.4	22.2	0.5	8.8
11	Carbonate-silicate-sulfate	6.9	0.6	45.7	5.8	..	4.5	31.6	0.4	5.6
12	Sulfate-silicate	6.4	0.4	34.3	8.0	..	44.0	1.7	..	4.3
13	Sulfate-silicate	6.0	4.2	31.8	9.2	..	43.4	0.2	..	6.6
14	Silicate	45.4	6.9	32.9	1.8	6.7	0.7	2.1	1.4	4.6
15	Silicate	48.3	2.5	29.9	3.2	5.7	2.8	2.2	1.6	5.2

* Hall, *Ind. Eng. Chem.* 17, 284 (1925).

TABLE 9.—*Analyses of Sludge and Scale Formed in Boiler.**

No.	Sample	Date taken	SiO_2	Fe_2O_3	CaO	MgO	Na_2O	SO_3	Moisture at 105°C.	Net ignition loss
			Percent							
1	Sludge in blow-down	June 16, 1922	12.7	25.3	13.8	10.6	0.6	19.3	1.0	15.1
2	Sludge in wash-back	June 16, 1922	11.4	22.2	12.9	15.3	2.1	19.0	0.7	19.3
3[a, c]	Sludge in blow-down	July 27, 1922	7.1	13.3	29.4	3.5	Not detd.	40.4	0.1	2.4
4[c]	Sludge in wash-back	July 27, 1922	37.1	15.9	1.4	20.0	" "	1.5	5.8	18.0
5	Scale, Boiler No. 1	October 10, 1922	1.5	2.2	38.6	1.6	" "	54.5	0.5	1.5
6	Loose sludge in mud drum of boiler ...	October 23, 1922	0.7	0.8	39.7	1.8	" "	56.3	..[b]	1.2

* Hall, *Ind. Eng. Chem.* **17,** 284 (1925).
[a] Much broken scale in this sample.
[b] Analysis made on sample dried at 105° C.
[c] A treatment of 15 pounds a day of sodium silicate was used when these samples were taken.

The temperature effects mentioned above may result in the formation of scales and sludge of very different chemical character in different parts of the same boiler. This is well illustrated by Paul in his very excellent treatise on Boiler Chemistry and Feed Water Supplies (2nd Edition 1923) from which we take the liberty of quoting at some length.

Examples.

The following water was used for feeding the boilers:

Feed Water.

	Grains per imperial gallon
Silica	.11
Oxide of iron	.10
Sulfate of lime	2.77
Carbonate of lime	.91
Carbonate of magnesia	.88
Chloride of sodium	2.46
	7.23
Hardness	4.00°

The result of using this water was the formation of a very considerable quantity of both scale and sludge.

	Scale from front of boiler	Scale from back of boiler	Sludge
	Percent	*Percent*	*Percent*
Silica	2.28	7.08	7.70
Oxide of iron	2.00	5.52	5.12
Sulfate of lime	75.38	30.63	27.25
Carbonate of lime	13.28	41.55	46.09
Magnesium hydrate	6.09	10.64	10.48
Organic matter	.97	4.58	3.36
	100.00	100.00	100.00

The sludge and the scale deposited on the back or cooler part of the boiler consists chiefly of carbonate of lime, while the scale from the front or hottest part consists principally of sulfate of lime. These three samples were taken from the same boiler.

The following are typical examples of purely carbonate scales:

Carbonate Scales.

Carbonate of lime	94.90
Magnesium hydrate	1.57
Oil	3.53
	100.00
Carbonate of lime	91.52
Sulfate of lime	3.67
Magnesium hydrate	1.57
Chloride of sodium	.18
Moisture	2.76
	99.70
Silica	1.90
Carbonate of lime	93.15
Phosphate of lime	.81
Carbonate of magnesia	4.14
	100.00

The first three samples are scales taken from the boiler itself, the last one from the feed pipes, hence the presence of carbonate of magnesia.

Although magnesia generally forms a fine floury deposit or sludge, sometimes it is found as a hard scale.

Magnesia Scale.

Silica	.86
Oxide of iron	.40
Sulfate of lime	12.71
Carbonate of lime	1.52
Magnesium hydrate	78.64
Organic matter, etc.	5.97
	100.00

Sometimes hydrate of magnesia is precipitated in a very beautiful form resembling silver spangles, and has been mistaken for aluminum paint, which it closely resembles. Analyses, however, show it to be artificial brucite (MgH_2O_2). The following is an analysis of a sample taken from a boiler where it had been deposited as a sludge:

Artificial Brucite.

Magnesium Hydrate	87.38
Silica	8.31
Alumina and oxide of iron	4.31
	100.00

The sample was dried before analysis, in the wet state it contained 31.13 percent of water over and above the water of hydration. When dried it still preserved its silvery appearance. This form of magnesia is only deposited from very dense boiler waters containing large quantities of magnesia and soda salts. The particular boiler water from which this sample was taken contained the following:

Boiler Water.

	Gr. per imp. gal.
Sulfate of lime	90.10
Sulfate of magnesia	445.95
Magnesium hydrate	10.96
Carbonate of magnesia	32.28
Nitrate of sodium	89.25
Sulfate of sodium	10,951.75
Chloride of sodium	2,211.30
	13,831.59

The following analyses give two sulfate of lime scales. One is the scale from the inside of the boiler, and the other from the outside of the condensing towers where the water was used for cooling.

Sulfate Boiler Scale.

Sulfate of lime	94.62
Magnesium oxide	4.20
Silica	.32
Oxide of iron	.24
	99.38

Sulfate Condenser Scale.

Silica	2.10
Oxide of iron	3.14
Sulfate of lime	68.10
Carbonate of lime	8.07
Water of hydration	18.03
	99.44

Sulfate scales are much harder than carbonate scales, they are non-porous and difficult to remove.

Silicate scales are even worse in this respect than sulfate scales, but such scales are not frequent, and when found are generally due to improper treatment of the water. Alkaline soda-waters dissolve silica somewhat freely, forming silicate of soda, and when this silicate of soda is boiled with a lime salt, an insoluble silicate of lime is precipitated and forms a very hard non-permeable and destructive scale. Silicate of magnesia forms a similar scale, and these scales, though often very thin, adhere so firmly to the iron that they are much more destructive than much thicker incrustations of sulfate and carbonate of lime. Silicate scales are also caused by the use of bad lime in treating the water.

The following is an example of silicate scale:

Silicate Scale.

Silicate of lime	63.03
Sulfate of lime	.32
Hydrated oxide of iron	36.53
	99.88

If the hydrated oxide of iron which exists in this scale as a distinct layer is eliminated and the analysis reconstructed, the percentage composition of the scale would be:

Silicate of lime	99.30
Sulfate of lime	.50
	99.80

which is practically pure silicate of lime.

Fine clays are also brought down by tropical rivers and as mechanical filtration is not effective, they often get into the boilers and cause a silicate scale. The following are examples from West Africa and South Africa:

West Africa.

Alumina and oxide of iron	11.17
Silicate of alumina	10.27
Silicate of lime	57.50
Carbonate of lime	14.10
Silicate of magnesia	3.13
Sulfate of lime	1.77
Organic matter	2.06
	100.00

South America.

Alumina and oxide of iron	11.17
Silicate of lime	34.41
Sulfate of lime	29.78
Carbonate of lime	21.02
Magnesia	.92
Organic matter	4.91
	100.00

This scale is extremely hard. It is almost impossible to remove it from the tubes by scrapers, and even when removed it is exceedingly difficult to pulverize it.

The following is an example of an artificial glauberite scale taken out of a boiler:

Soda Scale.

Silica	.69
Sulfate of lime	43.81
Sulfate of sodium	52.09
Magnesia	1.32
Water, etc.	2.09
	100.00

Scales are also often found containing very large percentages of the oxides of iron, but as the oxides of iron are derived from the corrosion of the boiler, they are not true scales. The following are examples of this kind of scale formed in a boiler evaporating a slightly acid water containing sulfate of lime:

Oxide of Iron Scales.

Silica	1.95
Oxide of iron	65.00
Basic ferric sulfate	3.00
Sulfate of lime	25.94
Magnesium hydrate	1.44
Water of hydration, etc.	2.67
	100.00

Silica	15.12
Ferrous oxide	14.97
Ferric oxide	32.29
Basic ferric sulfate	5.37
Sulfate of lime	23.12
Magnesium hydrate	8.35
	99.72

Oily Deposits.

Silica	5.45
Alumina and oxide of iron	18.68
Carbonate of lime	15.24
Sulfate of lime	.95
Magnesium hydrate	4.37
Organic matter	7.20
Oil	44.20
Moisture, etc.	3.91
	100.00

Carbonate of lime	42.00
Aluminate of lime	10.80
Oleate of lime	12.54
Oleate of magnesia	10.83
Silicate of magnesia	14.78
Oil	2.64
Moisture	6.41
	100.00

Foaming and Priming.

There is considerable confusion in the literature with regard to the exact significance of these two terms. They are sometimes used synonymously and sometimes with an apparent distinction in their meaning. Read [9] quoting R. C. Bardwell gives the following definitions:

> Foaming consists of the steam bubbles building upon the surface of the water, instead of breaking and freeing steam. It becomes serious when the bubbles build up so rapidly and hang together long enough to reach the point where dry steam is supposed to be taken off, starting a sort of siphoning action, and considerable water is carried over with the steam.
>
> Priming is the sudden evolution of steam from the heating surface, similar to "bumping" in laboratory apparatus, and is due either to poor design of the boiler and its being worked beyond its capacity, or to the sudden opening of the throttle. This is altogether different from foaming, and can be mechanically controlled to a large extent.

Similar definitions are given by Stabler.[10]

Foulk [11] suggests a third possible condition, namely, that the boiling may be "of such a character that the whole mass of water from the bottom up is full of fine steam bubbles with the consequences that the interior of the boiler is filled and much water passes out with the steam."

From what can be gathered from the literature the general opinion is that foaming is the more serious condition. Foaming is sometimes

[9] *Univ. of Texas Bull. No. 1752*, p. 40.
[10] *Loc. cit.*
[11] *Ind. Eng. Chem.*, **14**, 601, 1922.

attributed to the presence of soluble salts of sodium and potassium alone although Koyl (quoted extensively by both Foulk and Christie) showed quite conclusively by tests reported in 1900 and 1902 [12] that the presence of finely divided suspended matter was an essential second factor. The exact limit of concentration at which foaming occurs cannot be definitely set. In a locomotive boiler, railway water service men seem to be fairly well agreed, concentrations of 1700 to 2000 parts per million of non-incrusting salts may be allowed to accumulate in the boiler even when using a turbid water. For clear waters concentrations of more than 3000 to 3500 parts per million are not advisable. Concentrations as high as 13,000 to 14,000 have been used without difficulty in perfectly clear waters. Stationary boilers because of their greater relative size and less exacting conditions of operation are less troubled by foaming than are locomotive boilers.

More recently Foulk [13] has carried out a series of experiments determining under laboratory conditions the relation between concentration and foaming. He summarizes this investigation in his *Ohio Geological Survey Bulletin* as follows:

> Solutions of various compounds of calcium, magnesium, and sodium were boiled at pressures from 0.3 to 3.5 atmospheres, but in no case was a true foam produced. All of the substances, however, along with finely divided solid matter gave foaming mixtures.
>
> At least a hundred trials were made with various insoluble powders—pumice, sulfur, pyrolusite, bone black, lead sulfide, boiler scale, precipitated calcium carbonate, and limestone in boiling distilled water—but no appreciable foaming was observed.
>
> Any of these solids, however, if used in the solutions referred to above gave foams.
>
> Among the solids tried, pulverized boiler scale and limestone were the most effective foam producers. In the case of the boiler scale, the only solid tried in this experiment, it was found that foam-producing tendencies increased, equal weights of material being used, as the size of the particles decreased.
>
> In the case of the sodium salts, which were studied in some detail, a fair amount of foam was obtained with concentrations of 1000 parts per million if the amount of insoluble material was sufficient. Foaming increased with increasing concentration of the soluble material till about 7000 ppm. was reached. After that there was no change.
>
> Increasing the amount of insoluble material had the same effect as an increase in the concentration of the soluble salts. The one could therefore take the place of the other so that foams could be

[12] *R. R. Gaz.*, **32**, 663; **34**, 423.
[13] *Loc. cit.*

produced with a small amount of soluble material provided a large amount of insoluble solid was present, and vice versa. There was, however, a lower limit at about 500 ppm. for both soluble and insoluble material, that is, if the soluble salts were much less than this no reasonable amount of insoluble material would produce foam, and if less than this amount of insoluble matter was present no concentration of soluble salts was sufficient to make the liquid foam.

Experiments were made at pressures from about 0.3 to 3.6 atmospheres. No effect was observed except that at the higher pressures the foam bubbles were smaller and more nearly uniform in size and the boiling seemed to proceed more smoothly.

Solutions of substances like alcohol that lower the surface tension of water were tried and it was found that with a stabilizing agent, like finely divided solid matter, these solutions also gave foams.

By blowing air through a porous alundum crucible foams could be produced at room temperature, and it is worth recording that exactly the same relations held with these air-filled bubbles as with the steam-filled ones of the boiling solutions. Mixtures which foamed on boiling also foamed by blowing air into them at room temperature, and mixtures which did not foam on boiling also did not foam with air.

An effort was made to produce a solution that bore some resemblance to a boiler water containing "organic matter." To this end leaves and twigs were boiled with water and the solution filtered. Only two such solutions were made, the results being inconclusive; there was not much tendency to foam.

In the same paper Foulk calls attention to the fact that colloid chemistry has developed some theories on foam formation in general which are applicable to the question of foaming in boilers. He quotes the following statement on the conditions for foam production from Bancroft:[14]

To get a foam the only essential is that there shall be a distinct surface film, in other words, that the concentration in the surface layer shall differ perceptibly from that in the mass of the liquid. All true solutions will therefore foam if there is a marked change of surface tension with concentration, regardless of whether the surface tension increases or decreases. All colloidal solutions will foam if the colloid concentrates in the interface or if it is driven away from the interface. To get a fairly permanent foam the surface film must either be sufficiently viscous in itself or must be stabilized in some way. This can be done by introducing a solid powder into the same interface.

Solutions of aqueous alcohol, acetic acid, sodium chloride and sulfuric acid all foam when shaken; but the foam is unstable. Soap solutions foam when shaken and the foam is, or may be, quite stable

[14] *Applied Colloid Chemistry*, pp. 269-70.

owing to the viscosity of the soap film. With saponin the surface film is even more stable. If we add to aqueous alcohol some substance like lycopodium powder which goes into the interface, we get a stabilized foam. We can do the same thing with aqueous acetic acid by adding lamp-black. The presence of enough of a finely divided solid in the interface will make the film so viscous that the foam will be quite stable.

Foams may be considered as emulsions in which a gas is emulsified in a liquid instead of a liquid in a liquid. In the discussion of emulsions (p. 54), it was pointed out that Hildebrand had explained very satisfactorily the way in which different substances stabilize the film which maintains the emulsions. The effect of solid particles was found to depend upon the degree to which they were wetted by the liquid. The finely divided particles of earthy matter collect in the surface of bubbles of steam and prevent them from coalescing. But if a small amount of an oil is added which will coat the solid particles they will no longer be wetted by the water and cannot be held in the film about the bubbles of steam. Their stabilizing effect is thus destroyed.

Earlier theories attributed foaming to the surface tension of the solution but Millard and Mattson [15] have found no relation between foaming and surface tension. They experimented with water from a boiler which was giving trouble and from one which was steaming smoothly as well as with artificial solutions.

[15] *Ind. Eng. Chem.*, **17**, 685.

Chapter VI.

Economic Disadvantages of Unsuitable Waters —*Continued.*

Corrosion.[1]

Since corrosion must take place in the presence of moisture it may be considered as a dissolving of the metal even though the final product may be an insoluble coating or sludge. The change from an insoluble metal atom to a soluble metal ion is an oxidation reaction. The metal atom must lose an electron for each valence which it carries as an ion. The general reaction may be written

$$M^{\circ} - \ominus \rightleftarrows M^{+}. \qquad (1)$$

The factor which measures the tendency of the metal to lose electrons thus forming ions and going into solution is commonly referred to as the *solution pressure*, or *solution potential*, of the element. This solution potential has been measured for many of the metals by observing

TABLE 10.—*Solution Potential of Common Metallic Ions.**

Metal	Ion	Potential Volts
Aluminum	Al^{+++}	−1.28
Zinc	Zn^{++}	−0.76
Iron	Fe^{++}	−0.43
Lead	Pb^{++}	−0.12
Tin	Sn^{++}	−0.1
Hydrogen	H^{+}	**0.0**
Copper	Cu^{++}	+0.34
Silver	Ag^{+}	+0.79
Gold	Au^{+++}	+1.1

* Nernst, *Theoretical Chemistry.*

[1] This topic is approached with a strong sense of the impossibility of giving it adequate treatment in a limited space and by one who has not made a specalized study of the field. The following references have been found useful in the preparation of this material: Calcott, Whetzel and Whittaker, "Corrosion Tests and Materials for Chemical Engineering Apparatus," *Trans. Am. Inst. Chem. Eng.*, 1923; Pollitt, *The Causes and Prevention of Corrosion*, Van Nostrand, 1923; J. H. Paul, *Boiler Chemistry and Feed Water Supplies*, Longmans, 1923; and the more recent and extensive summary by Speller, *Corrosion, Causes and Prevention*, McGraw-Hill, 1926; as well as the bibliographies by Van Patten and Whittaker.

the voltage between a piece of metal in a molar solution of its ions and a hydrogen electrode in a molar solution of hydrogen ions. This method of determination makes the hydrogen the zero of the scale. The figures for some of the more common metals are quoted from Nernst's *Theoretical Chemistry* (see Table 10).

The metals above hydrogen dissolve in acids to liberate hydrogen under most circumstances. Those below hydrogen in the table do not. These data do not represent the true tendency for metals to dissolve in acids. After the first film of hydrogen is formed a certain additional voltage is required to cause a continuous liberation of gaseous hydrogen and solution of the metal. This is called the overvoltage. Table 11 gives overvoltage for various metals.

TABLE 11.—*Overvoltage of Certain Metals.**

Metal	Cathodic overvoltage H_2 in H_2SO_4 solution
Zinc	0.75 volt
Tin	0.49
Lead	0.42
Gold	0.36
Copper	0.33
Silver	0.29
Iron	0.27
Aluminum	0.19
Nickel	0.24
Platinum	0.17

* Me. Proc. Manchester Int., *Phil. Soc.*, **61**, Pts. II, III, Mem. 9.

Qualitatively at least, we may say that the higher the overvoltage, other things being equal, the less will be the tendency to corrode.

The combination of data from both tables explains certain apparent anomalies. Zinc, for example, stands above iron in the table of solution potentials, yet practically we know that a coating of zinc (galvanizing) will prevent corrosion. The overvoltage of zinc is practically equal to its solution potential so that pure zinc will not displace hydrogen after the first film is formed. Corrosion is arrested before it has gone far enough to be of consequence.

From the discussion thus far it may be surmised that hydrogen ions are the oxidizing agents in most cases of corrosion in natural waters. Writing equation (1) for the corrosion of iron in water (the case in which we are primarily interested) we have

$$Fe + 2H^+ \leftrightarrows Fe^{++} + H_2. \qquad (2)$$

But this reaction does not continue unless the hydrogen is removed. This may take place either by the application of an electromotive force

to overcome the overvoltage and cause the formation of bubbles of hydrogen gas or by the oxidation of the hydrogen to form water.

$$2H_2 + O_2 \leftrightarrows 2H_2O \qquad (3)$$

Reaction (3) takes place quite readily in the presence of such metallic catalysts as platinum black or palladium and may be assumed to be catalyzed by the corroding metal surface. Walker, quoted by

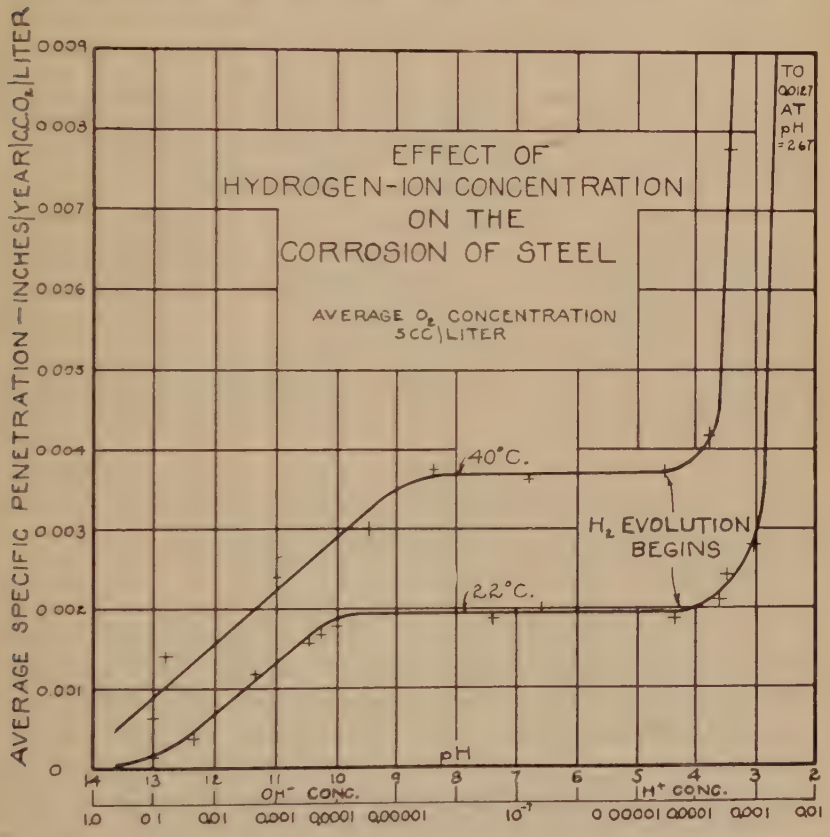


FIG. 8.—Effect of Hydrogen-Ion Concentration on the Corrosion of Steel (after Speller).

Speller,[2] has shown that in natural waters the *rate* of corrosion depends on reaction (3) rather than on reaction (2).

The popular over-emphasis of reaction (2) is due to a lack of understanding of the quantitative application of the law of mass action to the

[2] *Loc. cit.*

problem. If hydrogen-ion concentration alone is considered one would assume that the lower its concentration the less would be the corrosion but Wilson [3] has called attention to the fact that there are three zones in the pH corrosion curve. These are well illustrated in the curve by Whitman, Russel, and Altieri,[4] Figure 8, in which the effect of oxygen and pH on corrosion are both shown for waters in which there are no scale-forming substances present. The relative importance of different factors in corrosion varies with the zone. Wilson [5] classifies them as in Table 12.

TABLE 12.—*Relative Influence of Important Factors on Corrosion of Steel Immersed in Water.*

(Classified according to pH value and arranged in decreasing order of importance. Factors in parentheses are of minor importance.)

Alkaline Zone	Neutral Zone	Acid Zone
Corrosion Slow (pH greater than 10)	Corrosion Medium (pH from about 4.3 to 10)	Corrosion Rapid (pH less than 4.3)
Protective coatings	Oxygen concentration	Hydrogen-ion concentration
Oxygen concentration	Protective coatings	Hydrogen overvoltage
(Composition of metal)	Hydrogen-ion concentration	Composition of metal
(Hydrogen-ion concentration)	(Composition of metal)	Oxygen concentration
(Hydrogen overvoltage)	(Hydrogen overvoltage)	(Protective coatings)

This view explains to a large extent the apparent contradictions and disagreements as to the determining factors in corrosion. What one author has reported for one zone could not be expected to agree with what another has found in another zone.

Sources of Hydrogen Ion and Oxygen in Natural Waters.

While there are a great many factors which affect corrosion rates these two are always essential, the only exception being the relatively small effect of oxygen in the extremely acid range (pH less than 4.3) which is not commonly met with in natural waters. The sources of these two substances are therefore of prime importance.

Sources of Hydrogen Ion. Hydrogen ions may be present in neutral water in sufficient concentration to cause corrosion. This is demonstrated by the existence of neutral and even alkaline zone corrosion. Carbonic acid, H_2CO_3, when dissolved in water relatively low in calcium or magnesium bicarbonates, will furnish a hydrogen-ion concentration in the upper part of the acid zone. Various formulae have

[3] *Ind. Eng. Chem.* **15**, 127.
[4] *Ind. Eng. Chem.* **16**, 667.
[5] *See* Speller, *loc. cit.*, p. 26.

been suggested for calculating the hydrogen-ion concentration for waters containing bicarbonates from analytical data. They are all derived by applying the law of mass action to the equilibria involved, and differ mainly in assumptions as to the activity of the electrolytes. Baker and Greenfield,[6] assuming 85 percent for the activity and adding the value 1×10^{-8} for the hydrogen-ion concentration at the end point of the carbon dioxide titration, obtained the following:

$$[H^+] = \frac{4 \times 10^{-7} \times CO_2}{Alk} + 1 \times 10^{-8} \qquad (4)$$

and

$$[H^+] = \frac{3.5 \times 10^{-7} \times CO_2\ (\text{free})}{CO_2\ (\text{bound})} + 1 \times 10^{-8} \qquad (5)$$

where the amount of substance found expressed in parts per million is to be substituted for the chemical symbols.

The buffer effect of the bicarbonates may be seen in equation (4). Since the term for the alkalinity appears in the denominator it is obvious that for a given carbon dioxide content, the less the alkalinity the greater will be the hydrogen-ion concentration ($[H^+]$). Such formulae are based on the assumption of ideal conditions and are not to be used where actual determinations of the hydrogen-ion concentration can be made.

Tillmans[7] observed that the reaction

$$CaCO_3 + H_2CO_3 \leftrightarrows Ca(HCO_3)_2 \qquad (6)$$

did not go to completion but that there was a considerable amount of free carbon dioxide (H_2CO_3) remaining at equilibrium. The amount of carbon dioxide remaining was found to vary inversely with the amount of bicarbonate originally present. The portion of the free carbon dioxide in a water which would attack and dissolve ground marble ($CaCO_3$) Tillmans called *aggressive* carbon dioxide. In his book[8] Tillmans gives a table showing the amount of carbon dioxide in equilibrium with varying amounts of calcium bicarbonate from which the amount of aggressive carbon dioxide can be estimated. Auerback (cited by Tillmans) calculated the carbon dioxide at equilibrium in equation (6) but omitted several important factors. A more rigorous treatment of the problem has recently been given by Kolthoff,[9] in which the ionization constant, the corrected solubility of calcium carbonate and

[6] *Ind. Eng. Chem.* 12, 989.
[7] *Gesundheitsingenieur* 35, 669.
[8] *The Chemical Investigation of Water and Sewage*, p. 95.
[9] *Z. Nahr. Genussm.*, 41, 97; 43, 184.

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the ratio between calcium ion and bicarbonate ion (HCO_3^-) in the solution have all been taken into account. His formula for the carbon dioxide at equilibrium is

$$CO_2 = \frac{\alpha^3[HCO_3^-]^2Ca^{++}}{1.13 \times 10^{-4}}.$$

From a table of values for different concentrations of calcium ion and bicarbonate ion constructed from this formula the aggressive carbon dioxide may be determined by trial, remembering that each mol of carbon dioxide used in dissolving calcium carbonate reduces the free carbon dioxide available for equilibrium by a corresponding amount. The following data given by Tillmans will serve to illustrate the difference between free and aggressive carbon dioxide. A water containing 80 ppm. of bound carbon dioxide and 50 ppm. of *free* carbon dioxide showed 22.5 ppm. of *aggressive* carbon dioxide. Although this aggressiveness is measured against calcium carbonate it is considered by Tillmans to be a measure of the corrosive action of the water on metals. The aggressive carbon dioxide and the hydrogen-ion concentration of a solution of carbonic acid and carbonates will vary in the same direction as the bicarbonate concentration is changed.

The hydrolysis of such salts as magnesium chloride, calcium chloride, aluminum sulfate and ferric sulfate is an important source of hydrogen ions. The hydrolysis of the iron and aluminum salts will be discussed in Chapter VII.

The hydrolysis of magnesium chloride may form the connecting link in a continuous cycle of corrosion thus:[10]

$$MgCl_2 + 2H_2O \leftrightarrows Mg(OH)_2 + 2HCl \quad (7)$$
$$2HCl + Fe \rightleftarrows FeCl_2 + H_2 \quad (8)$$
$$FeCl_2 + Mg(OH)_2 \rightleftarrows MgCl_2 + Fe(OH)_2. \quad (9)$$

Or the ferrous chloride may be hydrolyzed

$$FeCl_2 + 2H_2O \rightleftarrows Fe(OH)_2 + 2HCl. \quad (10)$$

In all such reactions it must be borne in mind that the hypothetical combinations of ions shown in a boiler water analysis do not necessarily represent the compounds present in the boiler. Any water high in chloride ions may be corrosive due to the hydrolysis of some of the chlorides which may form under the conditions of concentration and pressure existing in the boiler. Nitrates, though less common, act in a similar manner.

Other less important sources of hydrogen ions have been reported;

[10] Speller, *op. cit.*, p. 407.

among them might be mentioned organic acids, either present in the water or formed as a result of decomposition of organic matter. Mineral acids, especially sulfuric and sulfurous acids are not infrequently found in mine waters and in streams carrying certain trade wastes. They may also be formed as the result of slow oxidation of hydrogen sulfide which is present in some waters.

Sources of Oxygen. Dissolved oxygen is the principal source of oxygen. Nitrates may also serve as sources of oxygen.

The solubility of the oxygen of the air is not very great—about 8 ppm. at ordinary temperatures—so that in a quiet vessel the oxygen may become exhausted in the vicinity of the corroding surface. It must then be replaced by diffusion which is a relatively slow process. Mechanical agitation will assist the replenishment of oxygen to the metal surface and thus aid corrosion.

Other Factors in Corrosion.

Aside from the hydrogen-ion concentration and oxygen concentration and the solution potential of the metal a large number of secondary factors have been observed to have a marked effect on the primary reactions. In many cases these secondary factors become so important as to actually determine whether corrosion will or will not take place under a given set of conditions. A discussion of these factors is beyond the scope of the present work. They are well summarized in Speller's "fourteen points." [11]

1. It is well known that iron will not corrode at normal temperatures in the entire absence of moisture.
2. The presence of oxygen is also essential if appreciable corrosion is to take place in ordinary water. Oxygen and water alone will cause corrosion even in the absence of carbon dioxide or other acids. In natural water, corrosion is almost directly proportional to oxygen concentration, if other factors do not change. Oxygen also accelerates the corrosion of iron in dilute acid solutions.
3. Corrosion in acid is much more rapid than in neutral solutions, and the latter is more rapid than corrosion in alkaline solutions.
4. Hydrogen gas is usually evolved from the surface of the metal during corrosion in acid solutions, but the evolution is very much less in neutral and alkaline solutions.
5. The products of corrosion include, mainly, black or green ferrous rust which forms next to the metal, and reddish-brown ferric rust which forms the outer layer, with graded mixtures of the two in between. When iron corrodes in the atmosphere the amount of

[11] *Ibid.*, p. 7.

ferrous rust is small, but when formed under water, the ferrous rust often amounts to as much as one-third of the corrosion products.

6. In corrosion in natural water, the precipitated rust usually carries down some calcium, magnesium, and silicious compounds, together with other insoluble material from the water. These substances have considerable influence on the structure and density of the rust coating on the metal surface. If the rust coating is loose and non-adherent, under ordinary conditions the rate of corrosion may be accelerated locally but, on the other hand, if it is uniformly dense and adherent, it may cut down the rate of corrosion very considerably.

7. In most cases, the initial rate of corrosion is much greater than the rate after a short period of time. This is particularly noticeable in alkaline solutions. As an exception, however, it should be noted that the initial rate of corrosion of a highly polished metal surface is abnormally low.

8. Corrosion is increased in dilute solutions of many neutral salts, but is decreased in more concentrated solutions, other things being equal.

9. In natural waters the rate of corrosion generally tends to increase with increase in the velocity of motion of the water over the metal surface.

10. Composition of the iron, within the ordinary variations found commercially, has little or no effect on corrosion under water, but sometimes it has a marked effect in atmospheric and acid corrosion. From the standpoint of corrosion, homogeneity of a metal is not usually so important as external conditions.

11. The condition of the metal surface in submerged corrosion may not affect the total corrosion, although it may have a marked tendency to localize the action.

12. Corrosion of iron is rarely uniform over the entire surface. Dissimilar metals in contact with each other, or with electrically conductive material in solution, tend to accelerate corrosion locally. This action is indicated by an electric current which flows through the solution from the more corrodible to the less corrodible material, i.e., from the anode to the cathode.

13. Variation in concentration or in composition of solutions in contact with a metal tends to localize corrosion at certain areas of the surface (i.e., accelerate it) and retard the action at others. When a portion of the metal in solution is protected from diffusion of oxygen, it becomes anodic to other areas which are in contact with a solution richer in oxygen, i.e., corrosion is more active at such protected areas. The smaller the anodic areas with relation to the associated cathodic areas, the greater is the rate of corrosion at the anodic points and the greater the tendency for the formation of small holes or pits.

14. The polarity of a certain area is often reversed during the progress of natural corrosion.

In addition to the foregoing, many other points have been deter-

mined and further significant facts are constantly being developed as a result of the wide interest in this subject.

Caustic Embrittlement.

In 1917 Parr [12] reported on an investigation of certain failures in boilers which he attributed to the action of caustic soda on the metal. The water used for boiler feed contained 60 to 70 ppm. of sodium carbonate which on heating hydrolyzed in part to form sodium hydroxide.

$$Na_2CO_3 + H_2O \leftrightarrows 2NaOH + CO_2.$$

The exact manner in which the caustic soda attacked the iron was not definitely determined but it was suggested that hydrogen was formed ($3Fe + 4OH^- \rightleftarrows Fe_3O_4 + 2H_2$) and dissolved in the metal, thus modifying its physical properties. The presence of sulfates was found to neutralize the effect of the caustic and prevent the embrittlement. A number of authors have stated that the embrittlement was the result of strains produced during the fabrication of the boiler. In answer to these claims Parr & Straub [13] have just completed an investigation which they summarize as follows:

> Three types of cracks are recognized: first, those due to direct corrosion of the metal; second, those due to fatigue; and third those which are caused by caustic solutions. Each is found to be distinctive in type, which makes it possible to recognize the embrittlement cracks when encountered. A study of the areas throughout the United States where embrittlement occurs has been made, but instances of embrittlement are noted which are the result of boiler water treatment. Hence, it is more important to know the condition of the water rather than the locality from which it comes, as an index of potential danger.
>
> A method of procedure was devised whereby the embrittlement effect could be produced at will, thus making it possible to study both the conditions under which it occurs and remedies for its prevention. The results indicate that two conditions must be present simultaneously to produce the embrittlement effect: first, the stressing of the metal above the yield point; and second, the concentration of sodium hydroxide to a point which is in excess of 350 g. per liter.[14] Parallel tests omitting the sodium hydroxide show no effect. Tests upon various types of metal from the purest obtainable to those with a high percentage of impurities show that impurities do not modify the conditions.

[12] *Univ. of Ill. Bull.* 94.
[13] *Ind. Eng. Chem.* **19**, 620 (1927).
[14] Later investigations by these authors indicate that 100 grams per liter of sodium hydroxide produces embrittlement.

Inhibition of embrittlement, so far as the experiments have gone, indicates that this might be accomplished by the elimination of localized stresses, which is assumed to be impossible. The modification or control of the chemical condition of the water has been found to be effective. Data on actual plants in use, covering a period of ten years, are consistent with the artificial embrittlement in that by maintaining a ratio of sodium sulfate to sodium hydroxide in excess of 2, no embrittlement is found to occur. Free sodium carbonate in the water is in itself not active in producing embrittlement, but contains a potential danger in that it gradually is hydrolyzed into the caustic form.

Photographs illustrating the cases of actual embrittlement in widely distributed regions, from Buffalo to Southern California, and from Michigan to Texas, show the wide distribution of the difficulty. Photomicrographs of both the natural and the artificially produced cracks furnish a method of identification as well as illustrate their special characteristics.

The high concentration of caustic (35 percent) found necessary for embrittlement would never be found in a boiler but may easily be reached in cracks and crevices. In fact, *solid* caustic has actually been found in such places. Parr is careful to state that sodium carbonate not only does not cause embrittlement but along with sodium sulfate tends to prevent it. It is only the sodium hydroxide which may be formed by hydrolysis of part of the carbonate which causes embrittlement. The general use of soda ash in boiler waters for many years and the extensive use without difficulty of zeolite softeners for boiler water treatment would indicate that in many cases the particular conditions for embrittlement which Parr has so clearly defined are not attained. An analysis of the boiler water will indicate whether they are being approached.

Presence of Iron, Manganese, Etc.

The presence of iron in a water is a serious disadvantage. When present to the extent of more than 0.1 to 0.2 ppm. it will cause rusty stains on plumbing fixtures or fabrics with which it comes in contact. It stimulates the growth of the so-called iron-bearing bacteria [15] to such an extent in some cases that distribution mains and meters become seriously clogged. According to the "colloidal theory of corrosion" the iron as it forms in a colloidal state acts as a catalyst in the oxidative corrosion of iron. In fact iron-bearing water is a disadvantage in practically every industrial or municipal use. For drinking purposes it

[15] See *U. S. Geol. Survey,* Professional Paper 113.

is not objectionable to most persons and is of advantage in cases of anemia.

The iron is generally supposed to be present in water as the ferrous carbonate or bicarbonate, $Fe(HCO_3)_2$. Exposure to the air even though it be brief results in the absorption of enough oxygen to cause oxidation to the insoluble ferric hydroxide or to a basic ferric salt. (Well waters ordinarily contain no dissolved oxygen.) In some cases, especially in mine waters or certain highly mineralized water, the iron is present as the ferrous sulfate. In these cases there is rarely enough acid present to keep the equivalent ferric salts in solution, so that aëration results in considerable precipitation from these salts as well.

The amount of iron in the water will naturally depend upon the chemical character of the stratum from which it is drawn. Two to three parts per million of iron are rather commonly found in many localities and 10 ppm. is not uncommon. A water having 130 ppm. of iron was recently reported by Bartow.[16]

Manganese occurs in waters to a greater extent than is generally appreciated. Corson and Bartow [17] give the following summary of the occurrence of manganese:

> The first water in this country in which manganese was reported in sufficient quantity to cause trouble was from a well supplying a New England mill in 1898. This supply was abandoned because of its high content of manganese. Sixty-two springs in the United States are listed by Mason [18] as having been reported to contain manganese. He states that nearly half of them contain only traces of the element and that only seven contain as much as the 4.5 parts per million which he found in a mineral spring at Excelsior Springs, Mo. Raumer [19] reports a water near Fürth which contained 6.2 parts per million of manganese. Bailey [20] states that the well-water supply of Hutchinson, Kans., contains 1.0 part per million of manganese.
>
> The trouble in Breslau [21] in 1906 is a classic example of injury to

[16] Private communication with the author.

[17] *Ill. State Water Survey*, Bull. **13**, 165.

[18] Mason, W. P., The manganese waters of Excelsior Springs: *Chem. News*, **61**, 123 (1890).

[19] Raumer, E. von, Ueber das Auftreten von Eisen und Mangan in Wasserleitungswasser: *Z. anal. Chem.*, **42**, 590-602 (1903).

[20] Bailey, E. H. S., Occurrence of manganese in a deposit found in city water pipes: *J. Am. Chem. Soc.*, **26**, 714-5 (1904).

[21] Woy, Rudolph, Störung der Breslauer Wasserversorgung durch Mangansulfat: *Z. öffent. Chem.*, **12**, 121-125 (1906); Kritische Besprechung der Erfahrungen mit der Breslauer Grundwasserversorgung: **13**, 401-411 (1907).

Lühriq, H., Über die Ursachen der Breslauer Grundwasserverschlechterung und die Mittel zu ihrer Behelung: *Z. Nahr. Genussm.*, **14**, 40-63 (1907).

Beyschlag, F., and Michael R., Über die Grundwasserverhältnisse der Stadt Breslau: *Z. prakt. Geol.*, **15**, 153-64 (1907).

Lühriq, H. and Blasky, A., Mangan in Grundwasser der Breslauer Wasser-

a water supply by very high contents of iron and manganese. Breslau was formerly supplied with water from Oder River, but in 1905 a supply was substituted from 313 driven wells 30 to 40 feet deep in Oder valley. In March, 1906, the Oder overflowed its banks, and soon afterward the turbidity, odor, hardness, residue, manganese, and iron in the ground-water supply enormously increased. The content of iron increased to 440 and the content of manganese to 220 parts per million. The filtered water from Oder River was necessarily substituted for the ground-water supply. Many explanations have been offered for this peculiar change in the quality of the water. Most authorities agree that it was caused by a process of oxidation and leaching of the soil, which contains a large amount of sulfides of iron and manganese. The iron sulfide was oxidized to iron sulfate by the dissolved oxygen of the river water. The water containing iron sulfate then percolated through the soil to the water-bearing strata, a part hydrolyzing to sulfuric acid which dissolved the manganese. Extensive experiments on the removal of iron and manganese from the supply have been carried on by a number of investigators.

Manganese waters at Björnstorp Estate, Sweden, are described by Weibull.[22] Pipes were clogged, and fabrics laundered in several waters from ponds and wells in the vicinity were turned yellow. Investigation showed that some of the waters contained as much as 6.3 parts per million of manganous oxide, or 5 parts per million of manganese which was precipitated upon exposure to the air. The rock formation in the vicinity is gneiss and diorite, the latter of which contains 8.2 percent of manganous oxide, which probably accounts for the high content of manganese of the waters.

A study of the content of manganese of waters in France has been made by Jadin and Astrug.[23] In several city supplies 0.0005 to 0.015 part per million of manganese was found. Mineral waters at Vichy and Boulon contained 0.09 to 0.20 part per million. The content of manganese of sources very near each other widely differed.

D. D. Jackson [24] has found an organism depositing manganese, *Crenothrix manganifera,* in the filter galleries of the city supply of Newton, Mass., the water of which contains 1.4 parts per million of Mn. He describes three species of organisms which form deposits in water systems, *Crenothrix kühniana* depositing iron, *Crenothrix manganifera* depositing manganese and *Crenothrix ochracea* depositing alumina from waters containing these elements. Analyses of the incrustations deposited show that they consist of about one-third silica,

leitung und die Frage der Abscheidung des Mangansulfates aus demselben: *Chem. Ztg.,* **31,** 255-7 (1907).

Weston, R. S., The purification of ground waters containing iron and manganese: *Trans. Am. Soc. C. E.,* **64,** 112-81 (1909).

[22] Weibull, Mats, Ein manganhaltiges Wasser und eine Bildung von Braunstein bei Björnstorp in Sweden: *Z. Nahr. Genussm.,* **14,** 403-5 (1907).

[23] Jadin, F., and Astrug, A., Le manganèse dans les eaux d'alimentation et les eaux minerals: *Compt. Rend.,* **157,** 338-9 (1913).

[24] *J. Soc. Chem. Ind.,* **21,** 681.

one-third organic matter, and one-third the oxide of the particular metal which the organism deposits. The author states that *Crenothrix kühniana* is very common, that *Crenothrix ochracea* is rather uncommon, and that *Crenothrix manganifera* is very rare, because manganese seldom occurs in sufficient quantity in water to produce a noticeable growth. *Crenothrix kühniana* is identical with *Crenothrix polyspora* (Cohn).

These authors found appreciable amounts of manganese in 12 out of 17 well supplies and 8 out of 50 surface supplies in Illinois. More recently Hawley and Mahle [25] have reported difficulties with manganese deposits in Breckenridge, Texas, from a water containing 0.036 ppm. manganese.

Manganese is said to occur as the manganous salt or oxide and, like iron, it precipitates on oxidation though apparently more slowly. The objectionable features of manganese are similar to those of iron.

An interesting case of clogging of water mains by growth of sulfur bacteria was observed by D. D. Jackson.[26] The water contained a considerable amount of hydrogen sulfide. Zinc has been reported in water due to corrosion of galvanized pipe in several instances. The corrosive action of soft waters on lead pipe is well recognized and has been the cause of lead poisoning. In some localities Public Health laboratories test all samples for lead as a matter of routine. The question of corrosion of lead is extensively discussed by Thresh.[27]

Disadvantages of Hard Water in Special Industries.

Canning.

Bigelow and Stevenson [28] have shown that hard water causes a toughening or hardening of peas and ripe beans and an incrustation of oxalates in beets, when used in the canning of these vegetables. They recommend water softened by the zeolite process for canning, since lime and magnesium are completely removed. Their experiments showed an adsorption of, or combination with, lime by the peas or beans when hard water was used.

Textile Finishing.

One of the chief disadvantages of hard water in the textile industry is the formation of insoluble compounds of lime with the soaps which

[25] *Eng. News-Rec.*, 90, 834 (1923).
[26] Private communication.
[27] *Examination of Water and Water Supplies.*
[28] *Nat. Canners Assoc., Bull.* 20L.

must be used in many of the processes. The lime soaps coat the fibers and render the cloth stiff and hard and sometimes spotted. In the dyeing end of the process these lime soaps may react unfavorably with either dyes or mordants or may coat the fibers and prevent them from taking the dye.

Tanning.

Lime and magnesium carbonate combine with certain of the chemicals used, more especially the tannins, causing considerable waste. Iron is also harmful since it causes stains and discolorations. Tanneries have found it worth while to soften water containing as low as 120 parts per million hardness before treatment.

Fermentation Industries.

In the fermentation industries the carbonates of calcium and magnesium are considered harmful but the calcium sulfate is found advantageous.[29]

Artificial Ice.

Artificial ice produced from hard water has a white or yellow sludge in the center of the cake. This sludge is caused by the freezing out or precipitation of the carbonates of calcium and magnesium as the water freezes. The sulfates and chlorides being more soluble do not form a sludge and may be removed by pumping out the "core." Agitation with air produces a better ice especially when the water is high in soluble salts. Behrman [30] gives the following statement concerning the allowable limits of soluble salts in ice manufacture. (The carbonates of calcium and magnesium can, of course, be removed completely by treatment.)

> Calcium sulfate, magnesium sulfate, calcium chloride, magnesium chloride, sodium sulfate, sodium chloride, and sodium carbonate all have, in general, the same effect on the appearance of raw water ice, and, therefore, in this rough tabulation, can be grouped together.
>
> Generally, the sodium carbonate can be considered 1¼ times as objectionable as the sulfates, and the chlorides about ¾ as objectionable as the sulfates. Therefore total the sulfates and chlorides separately and apply the factors:

[29] Warren, C. A., "Brewing Waters," *Brewing Trade Review*, London, 1923.
[30] Water Softening Bulletin of the National Lime Association, p. 35.

Total Sulfates	× 1.0 = ...	.....
Total Chlorides	× 0.75 = ...	.....
Sodium Carbonate	× 1.25 = ...	.....
Sum Total	=	.....

If sum total is less than 171 ppm. (10 gr. per gal.) first quality ice can be expected with efficient air agitation and average brine temperatures.

If sum total is more than 171 ppm. (10 gr. per gal. and less than 256 ppm. (15 gr. per gal.) good ice can be expected with slightly higher than average brine temperatures or slightly more than the usual volume of air for agitation.

If sum total is more than 256 ppm. (15 gr. per gal.) and less than 342 ppm. (20 gr. per gal.) merchantable ice can be made if much more than the usual volume of air per can per minute is provided, especially during the beginning of the freeze and brine temperatures of 18° or more are carried.

If sum total is more than 342 ppm. (20 gr. per gal.) and less than 684 ppm. (40 gr. per gal.) it is questionable whether merchantable ice can be made. Careful chemical investigation is advised.

If sum total is more than 684 ppm. (40 gr. per gal.) merchantable ice cannot be expected.

Paper Mills.

The size used in paper mills will combine with calcium and magnesium, causing a proportionate waste of this material. The salts of calcium and magnesium may be adsorbed on the pulp fiber and later cause trouble with the colors. Iron is especially objectionable because of its tendency to produce stains.

Miscellaneous Industries.

For glue factories, sugar refineries, starch works, concrete, various chemical works, etc., the quality of the water used is an important problem. Even a brief discussion of each case would lead into nearly every field of chemical engineering.

Chapter VII.

Industrial Water Treatment. Lime and Soda Process.

Of the various types of treatment which are applied to industrial water supplies, the one which remedies the largest number of defects is water softening. The removal of the salts of calcium and magnesium eliminates soap waste and boiler scale and in many cases leaves the water in a non-corrosive condition as well. Iron, manganese and silica are ordinarily removed along with calcium and magnesium by the softening reactions and the precipitation treatment removes turbidity.

The methods of water softening are ordinarily divided into two classes; pre-treatment, sometimes called external treatment, or the softening of the water before use, and internal treatment or softening in the boiler or laundry tub, that is, during use. There are two much-used methods of pre-treatment with a third of lesser importance. The oldest is the *lime* or *lime and soda* process of Clark [1] in which the impurities are precipitated as a sludge. A newer process but probably more widely used is the *base exchange* or *zeolite* system, frequently called *permutit,* because the first zeolite to be commercially exploited was given that name. Merely *heating* most hard water causes considerable precipitation but as a water softening process it can be used economically in only a limited number of cases.

Lime and Soda Process.

Chemistry of the Lime-Soda Process.

This process depends principally upon the relative insolubility of calcium carbonate and magnesium hydroxide. By the addition of the proper quantities of lime and soda ash (Na_2CO_3) these insoluble compounds are formed and the "hardness" thereby removed. The chemical reactions (omitting those for the chlorides and nitrates because of their similarity to those for the sulfates) are:

[1] *Repertory of Patent Inventions for 1841* (Great Britain).

$$H_2CO_3 + Ca(OH)_2 \leftrightarrows CaCO_3 + 2H_2O \quad (1)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftarrows 2CaCO_3 + 2H_2O \quad (2)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \leftrightarrows Mg(OH)_2 + 2CaCO_3 + 2H_2O \quad (3)$$

$$CaSO_4 + Na_2CO_3 \rightleftarrows CaCO_3 + Na_2SO_4 \quad (4)$$

$$MgSO_4 + Ca(OH)_2 + Na_2CO_3 \rightleftarrows Mg(OH)_2 + CaCO_3 + Na_2SO_4 \quad (5)$$

These reactions indicate a natural division of the salts causing hardness, into two classes, the *carbonates* (more strictly the bicarbonates) and the *non-carbonates*. The *carbonate hardness* requires the addition of lime for softening, while the *non-carbonate hardness* requires the addition of soda ash or in the case of magnesium salts, lime and soda ash (reaction 5). The term *temporary hardness* is sometimes used synonymously with *carbonate hardness* and *permanent hardness* as meaning the same as *non-carbonate hardness*. This usage is incorrect as has been shown by Buswell.[2] The term *temporary hardness* is of doubtful value at best. It is defined [3] as the hardness removed by boiling without any specification as to the length of time the boiling is to continue. The principal effect of boiling is to remove the carbon dioxide with the formation of carbonates.

$$H_2CO_3 \leftrightarrows H_2O + CO_2\uparrow$$

$$Ca(HCO_3)_2 \leftrightarrows CaCO_3 + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightleftarrows MgCO_3 + H_2O + CO_2\uparrow$$

Under these conditions calcium carbonate is only slightly soluble, about 20 parts per million, but magnesium carbonate is soluble to the extent of approximately 100 parts per million. Since 100 ppm. is more than the total magnesium hardness in many waters it is apparent that gentle boiling for a short time will not precipitate any of the magnesium carbonate hardness. "Temporary hardness" is also sometimes spoken of as being equal to the alkalinity. In the majority of waters there is the same objection to this use of the term that there is to using it as a synonym of *carbonate hardness*. In occasional cases where a natural water contains sodium bicarbonate this use of the term is even more objectionable. If temporary hardness = *carbonate hardness* = *alkalinity*, then the alkalinity of a sample of water should be reduced to approximately 30 ppm. by boiling. How far this is from the truth is shown by the following data:[4]

[2] *J. Am. Water Works Assoc.* **3**, 959 (1915).
[3] *Standard Methods, Am. Pub. Health Assoc.*, p. 27.
[4] Buswell, *loc. cit.*

Sample No.	1	2	3	4	5
Alkalinity before boiling.....	90	222	341	265	880
Alkalinity after boiling.....	63	110	90	170	345

The order in which calcium hydroxide reacts with carbonate ion was shown by Bartow and Lindgren [5] to be that in which the reactions are given above, except that in the case of waters containing sodium bicarbonate that salt reacts next after $Ca(HCO_3)_2$ and the following equation should be inserted:

$$2NaHCO_3 + Ca(OH)_2 \leftrightarrows Na_2CO_3 + \underline{CaCO_3} + 2H_2O \qquad (2a)$$

These reactions do not proceed to completion one at a time in the order given; there is rather a certain overlapping. The situation is more nearly as follows: [6]

The addition of calcium hydroxide increases the hydroxyl ion, thereby decreasing the hydrogen-ion concentration and displacing the carbonic acid-carbonate equilibrium (Fig. 21, Chap. X), which results in an increase first of the acid carbonate-ion concentration and with further addition an increase in the carbonate-ion concentration. At the same time the calcium-ion concentration is being increased by this addition of calcium hydroxide. When the product of the concentration of calcium-ion in the water originally plus the calcium-ion concentration added multiplied by the carbonate-ion concentration exceeds the value of the solubility product constant for calcium carbonate, then calcium carbonate will commence to precipitate. Reference to the discussion of aggressive carbon dioxide (Chap. V) indicates that the precipitation of calcium carbonate will commence before the amount of calcium hydroxide added reaches a value equivalent to the free carbon dioxide as reported by analysis, but not until somewhat more than the amount required to react with the aggressive carbon dioxide forming calcium bicarbonate has been added. The exact point may be calculated for any given set of conditions by the formula used by Kolthoff for determining the aggressive carbon dioxide making proper changes to allow for the fact that calcium hydroxide is used instead of calcium carbonate (marble).

The precipitation of calcium carbonate will continue with the addition of calcium hydroxide until all of the bicarbonates including sodium bicarbonate if present are converted to carbonates. As the carbonate equilibrium is shifted in the direction indicated there will be a rise in

[5] *Ill. State Pater Survey Bull.* 6, p. 33.
[6] *See* Buswell and Edwards, *Chem. & Met. Eng.* **26**, 826 (1922) and also Greenfield with Buswell, *J. Am. Chem. Soc.* **34**, 1435.

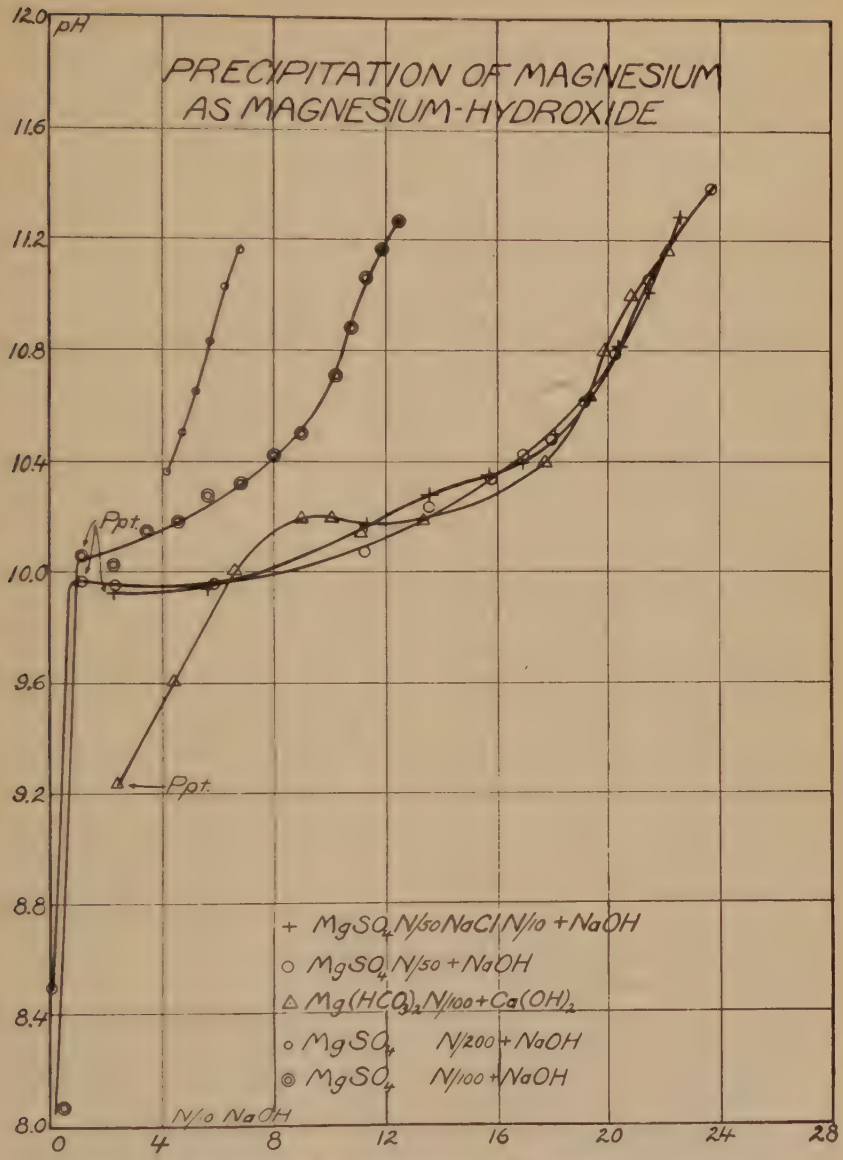


FIG. 9.—Precipitation of Magnesium as Magnesium Hydroxide.

the pH. When a pH of 10 or a little above is reached (*see* Fig. 9) the precipitation of magnesium ion as magnesium hydroxide may be expected. Below this point the magnesium will not precipitate except from

water of very high magnesium content, due to the solubility of magnesium carbonate. The hydroxyl-ion concentration will not ordinarily be sufficient to exceed the value required for the solubility product constant of magnesium hydroxide until after all of the carbonic acid and bicarbonate ion (including that equivalent to sodium bicarbonate if present) has been converted to carbonate ion.

In calculating the lime requirement these points must be borne in mind especially where partial treatment is desired or when sodium bicarbonate is present and magnesium ion is to be removed. It is sometimes desirable to remove only the calcium bicarbonate, since this can be accomplished with one equivalent of lime and the softening resulting per dollar's worth of chemicals is greater than in any of the other reactions. If magnesium is present the split treatment (addition of the total calculated amount of chemical to a portion of the water and then mixing with remainder of the flow) may not be used since the excess of lime will react with some of the magnesium. If the reaction time were sufficiently long the reaction would reverse on the addition of the second portion of raw water and the net result would be the same as with direct treatment. But the reversal of the reactions is so slow that it is scarcely detectable under operating conditions and the economy hoped for is not realized.

In the discussion of methods for the preparation of colloids (Chapter II) it was pointed out that substances of very low solubility form at such low total concentrations of their ions that there is little chance for the ultramicroscopic particles produced in the first stage of precipitation to increase in size either by recrystallization or aggregation, hence these substances tend to form sols. Magnesium hydroxide and to a lesser extent calcium carbonate fulfill these conditions so that it is not surprising that the addition of the calculated quantities of chemicals to a water does not always result in complete softening.

If reactions **(1)** to **(5)** proceeded exactly according to the above equations it should be possible to produce by this process a water of less than 30 parts per million total hardness. Johnson [7] gives the solubility of calcium carbonate as 17 to 20 ppm. and Buswell and Gallaher [8] give the solubility of magnesium hydroxide as 6.4 ppm. Theoretically the hardness after treatment should equal the sum of the two, calculated as calcium carbonate. The conditions under which these solubilities were determined are not ordinarily realized in practice, so that a residual

[7] *J. Am. Chem. Soc.* **37**, 2001-20 (1915); **38**, 947-75 (1916); **38**, 975-83 (1916).
[8] *Ill. State Water Survey Bull. 22.*

hardness of 50 to 70 ppm. is to be expected under good operating conditions.

In the curve showing the relation of pH to the precipitation of magnesium hydroxide (Fig. 9) it will be noted that the pH drops slightly as the precipitate begins to form; this could occur under two conditions as pointed out by Greenfield and Buswell.[9]

> It is especially noticeable that the curve for the titration of magnesium bicarbonate solution with lime water passes a maximum in the neighborhood of pH 10. Since the reactions are complicated at this point it is difficult to assign an explanation. The solution is undoubtedly depositing both calcium carbonate and magnesium hydroxide. It is also probable that magnesium carbonate is being deposited. One explanation that might be offered is that one of the precipitates changes its physical state. That is, if one of the precipitates were colloidally dispersed it would probably have a solubility somewhat greater than the same substance would have in a non-colloidal state. If a certain hydroxyl-ion concentration should cause coagulation there might result a decrease in solubility and a corresponding decrease in the pH.

This explanation assumes that the coagulated precipitate is not peptized by the decrease in hydroxyl-ion concentration, which is not improbable, as it is well known that these colloidal reactions are often not reversible in the strictest sense of the word. It is also true that while the formation of this maximum in the neighborhood of pH 10 is most noticeable in the case of the carbonate solution, it is noticeable to some extent in most of the other experiments.

Or the magnesium might form a basic salt, e.g., $Mg_4(OH)_2(CO_3)_3$, which is more soluble than the hydroxide and then at a certain excess of OH^- change over rapidly to the hydroxide with a resulting decrease in pH.

The basic carbonate formation is favored by Hoover,[10] who states:

> The difficulty in obtaining a complete reaction between the lime and soda-ash with calcium and magnesium salts in the water seems to be due to the fact that the soda-ash combines with the magnesium salts and forms complex basic carbonates or a complex double salt of sodium, magnesium, basic carbonates or perhaps colloidal precipitates of these salts. These salts may be represented by the following formulae:

$$Mg_4(OH)_2(CO_3)_3$$
$$MgCO_3.NaHCO_3.4H_2O$$
$$MgCO_3.Na_2CO_3$$

[9] *Loc. cit.*
[10] 1925 *Report of the Division of Water, Columbus, Ohio.*

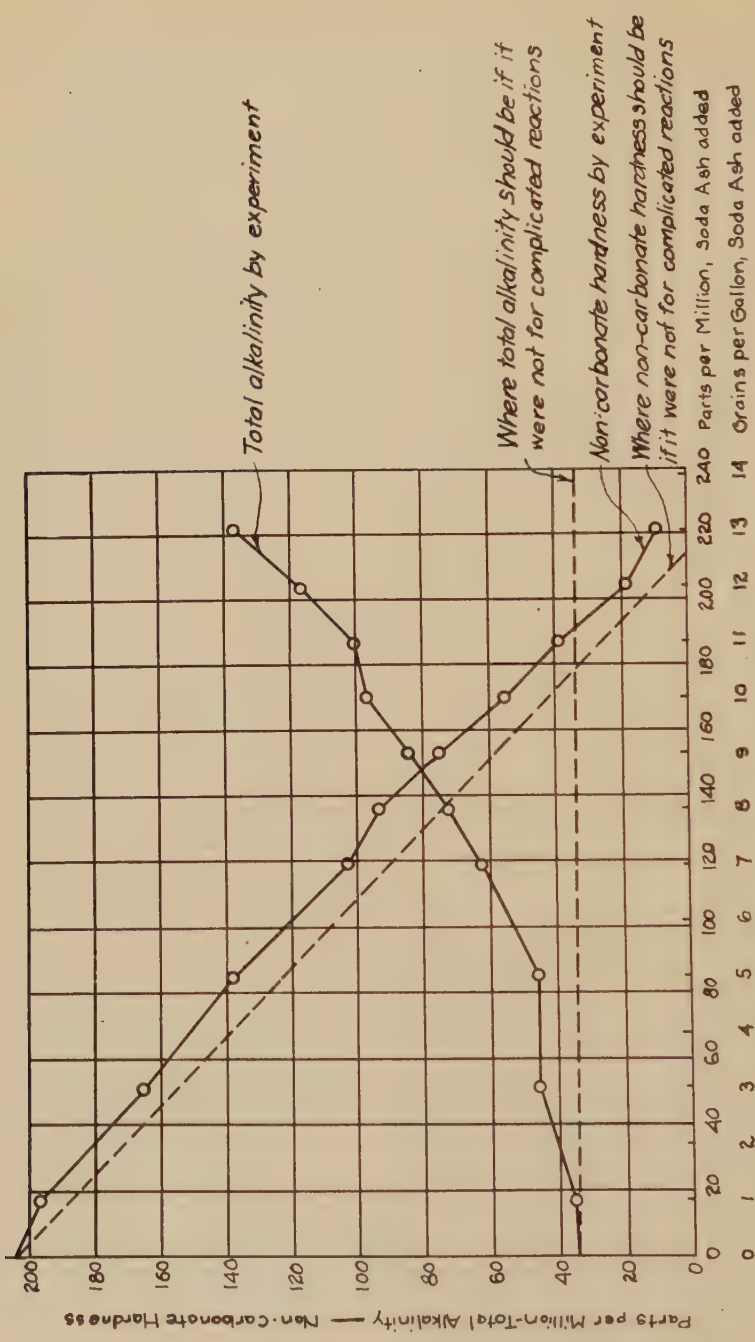

Total alkalinity by experiment
Where total alkalinity should be if it were not for complicated reactions
Non-carbonate hardness by experiment
Where non-carbonate hardness should be if it were not for complicated reactions
Parts per Million, Soda Ash added
Grains per Gallon, Soda Ash added
Parts per Million—Total Alkalinity —— Non-Carbonate Hardness

FIG. 10.—Residual Hardness in Scioto River Water at Columbus, Ohio (after Hoover).

Water that is high in non-carbonate hardness is more difficult to soften than water with an equivalent amount of hardness but low in non-carbonate hardness, because non-carbonate hardness requires soda-ash for its removal and large amounts of soda-ash are conducive to the formation of these basic carbonates.

The chart opposite (Fig. 10) shows by curves the change of the alkalinity and non-carbonate hardness of a magnesium water when treated by the lime soda-ash method. The non-carbonate hardness should decrease along the broken diagonal theoretical line, thus showing that the theoretical calculated amount of non-carbonate hardness is not removed. The alkalinity should remain constant and follow the broken horizontal theoretical line on the addition of soda-ash; instead, the alkalinity rises along the circled line above the theoretical line. This behavior is characteristic of magnesium waters regardless of whether the magnesium is in the form of sulfate, chloride or other radical. It is believed that the portion of soda-ash not going to remove the non-carbonate reacts with the magnesium salts in the water forming complex basic salts.

In the discussion of Von Weimarn's theory referred to in Chapter II, it was pointed out that sols could be precipitated or their formation prevented (1) by increasing the rate of diffusion between the insoluble particles—this may be accomplished by raising the temperature or increasing the concentration of the precipitant; (2) by increasing the chance of contact between particles thus increasing the growth in size of particles by aggregation—this can be done by stirring (mechanical or by heat) or by filtration or the addition of suspension of solid particles large enough so that they will settle through the liquid; and (3) by the addition of some reagent which will break or decompose the solution link of the colloidal particles.

"Excess treatment" is recognized as a method of "forcing" the precipitation to completeness by the addition of an excess of precipitants. It has been more popular in railroad work than elsewhere. The excess of lime and soda is added to such an extent that the alkalinity of the treated water is 2 grains per gallon higher than the hardness and the phenolphthalein titration is 1 grain per gallon more than half the total alkalinity. A water of 34 ppm. (2 gr. per gal.) hardness can be produced in this way.

A modification of the excess treatment is the split treatment described by Hoover [11] as follows:

> The addition of excess chemicals tends to prevent the formation of these basic carbonates, but in softening water for the city of Columbus, the use of excess treatment is not regarded as advisable

[11] *Loc. cit.*

because of the increased cost and it is felt that too much excess treatment might influence the natural taste of the water so softened; therefore, a modification of the excess treatment has been employed, and it is known as the split treatment process. Briefly, this consists of overtreatment with lime and soda-ash of as large a portion of the hard water as possible to get the maximum reduction of hardness and then neutralizing the excess lime and soda-ash with raw water.

The split treatment process reduces the hardness of a given quantity of raw water with a given quantity of chemicals more than the same quantity of chemicals will when added in the usual way, but it is not as effective in reducing hardness as overtreatment.

One of the most effective means of removing the lag phase in the precipitation of magnesium is the use of aluminum sulfate. The effect of the alum on the alkalinity is out of all proportion to that calculated from stoichiometric relations and appears to be that of the coagulation of a colloid. The advantage of using alum or copperas especially with high magnesium waters has been recognized by specialists in this field for a great many years but the reactions involved have been neglected by many authoritative works on water softening. In the *Report of the Division of Water of Columbus, Ohio, 1913,* Hoover gives some data on the subject:

Sulfate of alumina is ordinarily used as a coagulant but this plant has also used it to reduce the carbonate hardness of the water. From ½ to 1 grain of alum added to the settled water before it goes to the filters will reduce the alkalinity from 20 to 30 parts per million, whereas theoretically 1 grain of alum should only reduce the alkalinity about 8 parts per million. The ability of a coagulant to reduce these carbonates would indicate that perhaps they are present as colloids and that the flocculent precipitate formed by the addition of the coagulant drags them out.

It is also probable that the aluminum ion breaks the solution link of the negative magnesium hydroxide and calcium carbonate particles. The reactions of alum are discussed in some detail in Chapter X.

Recent experiments indicate that the use of sodium aluminate assists in water softening probably by forming a very insoluble magnesium aluminate.

Stirring has been found very useful in decreasing the time required for completion of precipitation and devices for returning a portion of the sludge to the point where the chemicals are introduced have been used in water softening for a great many years. Both of these devices increase the chance for a colloid particle to come in contact with another colloid particle or a larger particle with the resultant formation of clumps large enough to settle out. With these mechanical aids a mini-

mum of 4 hours is advisable for reasonably complete precipitation and a twelve-hour sedimentation period is recommended where it is feasible.

Even with a long sedimentation period a considerable amount of "colloidal" alkalinity or hardness remains in the water. This colloidal hardness precipitates out slowly and will cause incrustation or scale in the distribution system.[12]

To prevent this after-deposit sand filters are now generally used especially in connection with the larger softening plants. The effect

FIG. 11.—Miami, Florida, Water Softening Plant (Mixing Tank and Dorr Clarifier).

of the filters is to increase the chance of contact between colloidal particles and to furnish an extensive surface to which the colloids will stick. (A further discussion of filtration will be found in Chapter X.) The sand grains become incrusted with the calcium carbonate and magnesium hydroxide which they adsorb, and eventually must be discarded. At Columbus, Hoover found this increase in size to be 150 percent in nine years.[13] Sperry[14] found colloidal magnesia responsible for most of the clogging and incrustation at Grand Rapids although many reports give the composition of the incrustation as largely calcium carbonate.

The effect of the different steps in the water-softening process may

[12] Weston, *Eng. News* **59**, 188; Koyl, *Eng. News-Rec.* **86**, 458; and Hoover, *loc. cit.*

[13] *Eng. News-Rec.* **78**, 250.

[14] *Ibid.*, **78**, 304.

be judged from a summary of eleven years records on the Columbus, Ohio, plant. Ninety percent of the precipitation occurs in the mixing basin, three percent in the fifteen hours in the sedimentation basin and seven percent in passing through the filters.

In many municipal softening plants using surface sources of supply the softening process is really secondary to the treatment of the water for the removal of bacteria, turbidity, etc. (Chap. X). The incrustation of the sand by calcium carbonate and magnesium hydroxide greatly impairs the efficiency of the filters and is a serious matter in such cases.

(Courtesy C. P. Hoover)

FIG. 12.—Piqua, Ohio, Water Softening Plant.

Re-carbonation.

When the protection of the filter is more important than the removal of the last portion of the hardness, back treatment with acid of some sort is the obvious solution to the problem. Such treatment will increase the final hardness of the water since acidification will convert the calcium carbonate and magnesium hydroxide into soluble compounds and after-deposits and incrustation of filter sand will be effectively prevented. The acidification need not be carried far enough to produce a corrosive or aggressive water. The bicarbonate stage is far enough. The first attempt at this sort of treatment appears to have been at Owensboro, Ky.[15] More extensive investigations have been made by Hoover.[16]

The cheapest acid is of course sulfuric, but because of its high ionization and the consequent large effect of a slight excess on the pH

[15] Briedenbach, *Proc. A. W. W. A.*, 1912, p. 203.

[16] *Third Report Ohio Conf. on Water Purif.*, p. 62, and other references by this author cited.

treatment plant operators have been reluctant to use it. Phosphoric acid was tried by Hoover but later abandoned because of the cost. Carbonic acid has several points in its favor and is the one at present employed for back treatment. It is the acid normally present in natural waters and hence can cause no objection on the part of the layman, its ionization is so low that a considerable excess affects the pH only slightly, and it can be introduced into water with comparative ease and it is not particularly expensive.

Of the various well-known sources of carbon dioxide Hoover recommended flue gases at first, since where water is pumped by steam power more than enough carbon dioxide is produced in the generation of steam to carbonate the water pumped. The dust and sulfur were fairly easily removed from flue gases by scrubbers but apparently the phenols were not easily removable and caused tastes especially when the water was chlorinated (*see* Chap. X). This source of carbon dioxide was therefore abandoned.

When coke, which has been treated long enough in the retorts to expel all tar, is burned satisfactory carbon dioxide is obtained. N. S. Hill [17] describes in detail the construction of a coke burner and carbonator at Defiance, Ohio, and H. T. Campion [18] gives the following account of the operation of the same plant.

> During the year just past, complete carbonization of the lime-softened water leaving the settling basins has continued practically without interruption. The water delivered to the consumers has had an average content of from one to five parts per million of free carbon dioxide. The results of the carbonation treatment are well shown by the following table giving the averages of daily tests throughout the period of one year for alkalinities and free carbon dioxide content in settled and carbonated water.

TABLE 13.—*Results of Re-carbonation Treatment.*
(*Year's average of daily tests.*)

	Settled water (before carbonation) ppm.	Filtered water (after carbonation) ppm.
Alkalinity (total by methyl orange)	52	53
Basicity (monocarbonate alkalinity)	42	0
Causticity (hydrate alkalinity)	10	0
Free Carbon Dioxide	0	2.5

> The amount of coke burned during the year in the production of the carbon dioxide gas was 24.7 tons. Approximately the same

[17] *J. Am. Water Works Assoc.* **11**, 393.
[18] *Third Report Ohio Conf. on Water Purif.*, p. 39.

amount was used the year previous. Expressed in terms of water treated, 200 pounds of coke have been used per million gallons, representing an increase in rate over last year because of the greatly decreased water consumption. It has been found impracticable to maintain a fire in the furnace constantly with any smaller quantity of coke. The cost of coke used was $12.50 per ton or $1.29 per million gallons of water treated.

A table given by Hill shows the effectiveness of back-treatment with carbon dioxide in preventing incrustation of sand. The sand from Grand Rapids, where no back-treatment is used, is compared with that at Defiance.

(Courtesy C. P. Hoover)

FIG. 13.—Dorr Clarifier at Piqua, Ohio.

TABLE 14.—*Comparison of Grand Rapids and Defiance Sands.**

	Defiance original sand	Defiance sand, average, in use 15 mo.	Defiance sand, average, in use 21 mo.	Grand Rapids original sand	Grand Rapids in use 2 mo.	Grand Rapids in use 22 mo.
Efficient size 60%	0.43	0.49	0.49	0.35	0.42	0.51
finer than uni-	0.63	0.62	0.62	...	...	...
form coefficient.	1.5	1.27	1.26	1.25	1.33	1.22

* Hill, *J. Am. Water Works Assoc.*, 11, 393.

The amount of carbon dioxide required is given by Hill as 3 to 5 parts per million. From Kolthoff's formula or Tillman's tables (*see* Chap. V) the calculated amount of free carbon dioxide required to maintain equilibrium in a water having carbonate hardness of 80 ppm. is approximately 2 ppm. The treatment used by Hill would therefore give an excess of from 1 to 3 ppm. of aggressive carbon dioxide.

The addition of carbon dioxide lowers the pH of the water but to what extent the available reports do not state. In case alum is used

as a coagulant along with the lime and soda, this lowering of the pH will favor alum coagulation (*see* Chap. X). This effect has been observed by Campion.[19]

Apparatus for Lime-Soda Process.

Apparatus for lime-soda softening is of two general types, the intermittent and the continuous. The intermittent type consists of tanks of sufficient size and number to provide the amount of softened water required. The tanks are filled in succession and dosed with the predetermined amounts of chemicals. A brief period of agitation follows the addition of the chemicals and the precipitate is then allowed to settle, usually for a 12 to 24-hour period. The clear water is decanted through a filter for use.

The continuous softeners vary considerably in construction depending upon the size and make of the apparatus. The smaller machines for factories and power plants are usually steel tanks with an inner conical or cylindrical well. The lime and soda are fed as a heavy suspension or milk, the rate of flow of chemicals being automatically controlled by the flow of hard water. The raw water and chemicals flow into the central well where they are mixed. The flow is downward through this central well and upward through the annular space between the well and tank wall. The size of the tank is usually such as to provide 4 to 6 hours for reaction before the treated water is drawn off through a filter for use. Obviously the accurate adjustment of the chemical feed is essential to this type of machine.

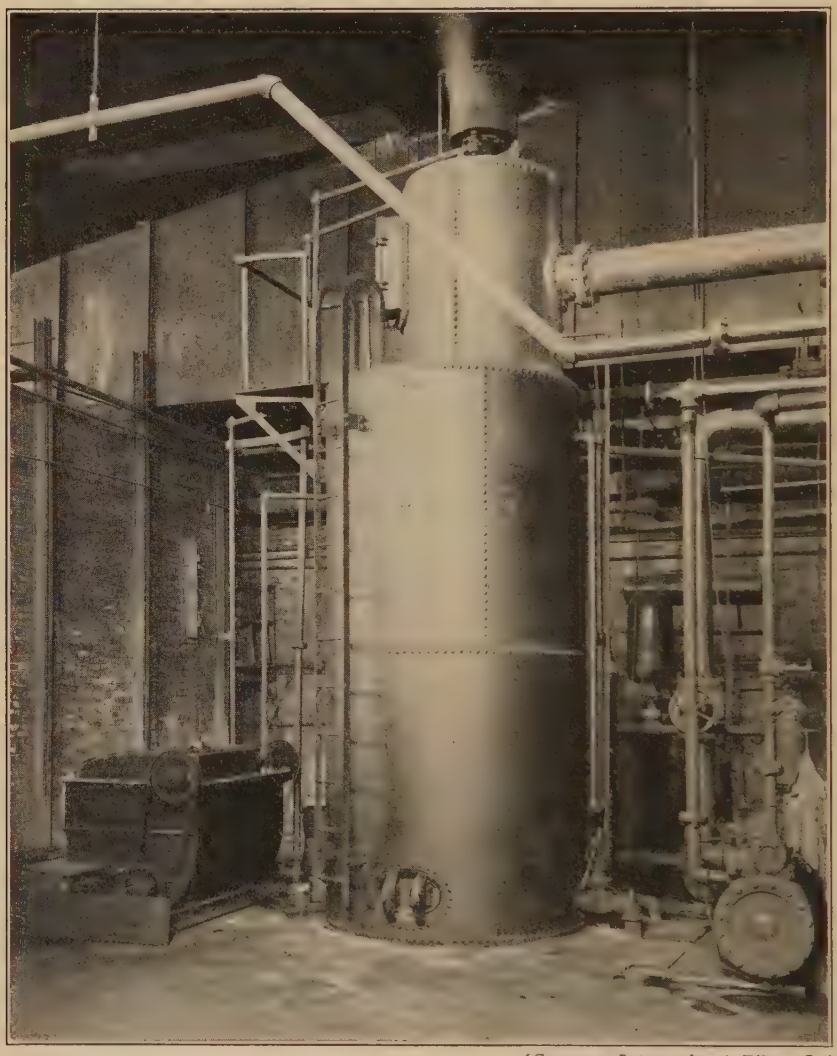
The large municipal softening plants resemble ordinary filter plants, with their chemical dosing devices, mixing chambers, sedimentation chambers and filters. Because of the large volume of sludge to be handled the preliminary sedimentation chambers have been provided with Dorr clarifiers in most of the newer plants. The clarifier chamber is shown in the illustrations (Figs. 11 and 13). With this device the concentrated sludge is removed continuously and a portion returned to assist in coagulation. Present data[20] indicate that the clarifier removes 96.2 percent of the settleable solids in the Newark, Ohio, plant.

Hot Process.

When water is softened for boiler feed it is to be heated eventually, so it is advantageous to heat it prior to the addition of the softening

[19] *Loc. cit.*
[20] *Eng. News-Rec.* **92,** 487.

reagents. The effect of heat is to increase the rate of crystallization in three ways; (1) convection currents cause stirring, (2) the rate of dif-



(*Courtesy International Filter Co.*)

FIG. 14.—Hot Process Softener Installation.

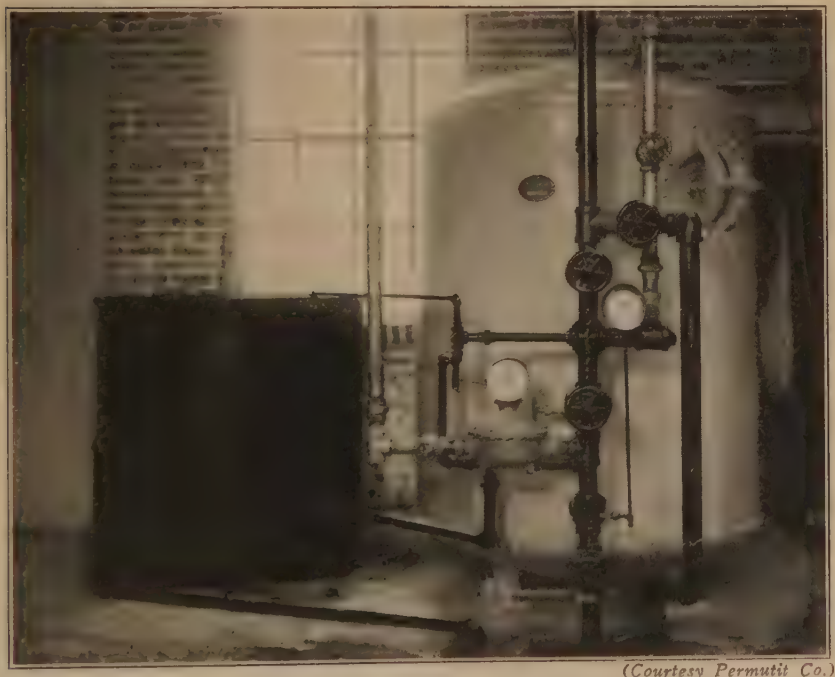
fusion is increased and (3) the viscosity of water is decreased. These conditions lessen the tendency for the formation of colloids and increase the rate and completeness of precipitation (p. 48). An effluent of 30 to 35 parts per million hardness may be obtained in less than an hour by this process.

Chapter VIII.

Industrial Water Treatment—*Continued.* Zeolite Process.

Definition of the Zeolite Process.

The zeolite softening process depends upon the fact that certain complex compounds of sodium, aluminum or iron, and silicon with oxygen and water possess the property of *base exchange*. That is, the



(Courtesy Permutit Co.)

FIG. 15.—Zeolite Water Softener.

sodium of the compound is replaceable by other metal ions if brought into contact with their solutions and what is of equal importance the reaction is reversible if the concentrations are changed. These compounds exist in nature as members of the class of minerals known as

the zeolites and are also manufactured artificially under various trade names. For water softening these zeolites are prepared in granular form and used instead of sand in an ordinary filter.

Early History of Zeolites.

The early history of zeolites has recently been covered by Behrman:[1]

The father of the base-exchange idea was an Englishman, J. Thomas Way, Consulting Chemist to the Royal Agricultural Society. In 1850 and 1852 Way presented two classic papers before the Society on the "Power of Soils to Absorb Manure."

Mr. Way mentioned "that he had found that soils have the faculty of separating ammonia from its solution: a fact appearing still more extraordinary, inasmuch as there is no ordinary form of combination by which we could conceive ammonia to be combined in a state of insolubility in the soil."

Then came his important series of experiments in which he treated the soil with solutions of ammonium sulfate, and found in the filtrate "an abundance of sulfuric acid in combination with lime."

As a result of the experiments reported in his first paper, Way concluded that this power of base-exchange, or the "power to hold manure" as he termed it, was due to clay.

In his second paper he tried to isolate the particular and responsible constituent of the clay. He was satisfied that there was such, and he hoped to be able to produce it artificially. He did.

This responsible constituent was evidently a lime compound, since lime compounds always appeared in the filtrate. Since soils contain large quantities of silica, it was reasonable to suppose some calcium compound of silicic acid might be the substance sought. So he prepared calcium silicate by precipitation and tried it. The result was negative.

Thereupon, he abandoned the idea of simple silicates, and turned his attention to the double silicates present in clay. He tried feldspar, the double silicate of alumina and potash, and albite, the double silicate of alumina and soda. Again the results were negative.

In spite of this discouragement, he still persisted along this line. To use his own words, "it was still possible, however, that these double silicates, when formed artificially by precipitation, might be capable of effecting that which in the mineral state they were unable to accomplish."

So he made these "double silicates artificially . . . by precipitation." For his experiments he prepared a double silicate formed by the action of sodium aluminate on sodium silicate. This product was the answer to his problem. The constituent of clay responsible for base-exchange—for "absorbing manure"—had been found.

It would be unfair, however, not to point out the one important flaw in Way's conclusions relating to base-exchange. He decided

[1] *J. Am. Water Works Assoc.* **13**, 221.

that there was a definite preference and order in base-exchange and that, beyond this, the process was not reversible. He drew up a series of bases—soda, potash, lime, magnesia, and ammonia—much in the manner of the electromotive series of metals. In this series, any base would be dislodged by any one following it in the list, but the action would not be reversible.

This was corrected a few years later by Eichhorn.[2] He showed that the bases were mutually exchangeable. He definitely established also the base-exchange properties of the natural zeolites, which are hydrated double silicates, and pointed out that Way's unsuccessful experiments with natural materials were due to the fact that he used anhydrous double silicates.

In Way's and Eichhorn's conclusions we have the essential theory of base-exchange as we use it today in water softening. We really have not advanced appreciably beyond this.

The earliest suggestion as to the possible commercial or industrial application of the base-exchange power of the zeolites was made by Way himself, who thought that they might be used as fertilizers. This has never come to pass, with the possible exception of glauconite or greensand; and this is used as a fertilizer to a limited extent, more for its potash content, as such, than for the manner in which this potash is combined.

The first real attempt to utilize zeolitic materials industrially was in the beet sugar industry. The idea was that, if the potassium compounds in the sugar juices are replaced by calcium compounds, the yield of crystallizable sugars is materially increased. Credit for the idea of using the base-exchange power of the natural zeolite was claimed by Rümpler, though the first patent covering the process was issued to Harms.[3] Harms used as a base-exchange material a silicious earth.

A little later, Rümpler,[4] also working with the removal of potash from sugar juices, demonstrated the base-exchange power of cement. He also carried out the purification by means of synthetic material he precipitated in a porous medium like charcoal. Rümpler pointed out that if the zeolites were regenerated with sodium compounds, in place of calcium compounds, they would extract calcium, magnesium and potassium from solution.

The next step in the development of zeolites is due to the work of Gans, which is summarized by Duggan.[5]

Gans[6] has divided the zeolites containing aluminum into two classes:

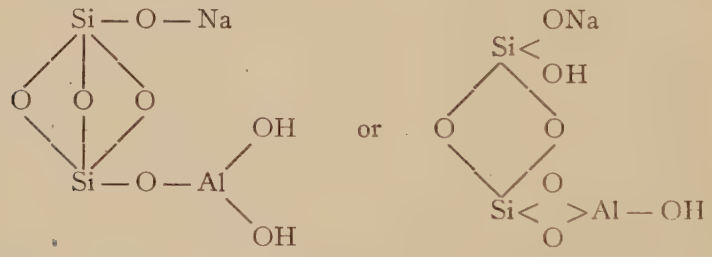
1. Zeolites which contain the alkaline earths and alkalies mostly combined with silicic acid, the bases of which can only be substituted

[2] *Pogg. Ann. Physik u. Chem.* **15,** 126-133 (1858).
[3] Ger. Pat. No. 95,447, June 2, 1896.
[4] *Deut. Zuckerind.*, **26,** 585 and 625 (1901).
[5] *8th International Congress of Applied Chemistry*, **25,** 125.
[6] *Annual Reports of the Royal Prussian Geological Institute*, 1905-1906.

in a very small proportion within a given time. These he summarily described as "double silicates of aluminum." The alumina and the alkali and alkaline earth base each substituted uniformly one hydrogen of the hydrate of silicic acid.

2. Zeolites which contain the alkaline earths and alkalies combined principally with alumina, and which substitute their bases nearly completely within a very short time. Gans called these "aluminate silicates." They are known commercially as "Permutit" as this description is best suited to describe their nature. The bases in these silicates are for the most part combined with the silicic acid by means of hydrate of alumina, one or two of the hydrogens of silicic acid being substituted by the group Al(ONa)OH, or less likely perhaps the group Al(ONa).

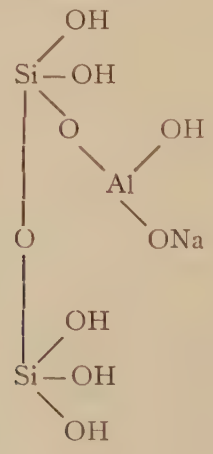
The double silicate of alumina of the first group would be analcime, with the formula: $Na_2Al_2Si_4O_{12} + 2H_2O$, which could be expressed graphically thus:



Chabasite belongs to the second class, with the formula:

$$Na_2Al_2Si_4O_{12} + 6H_2O,$$

which could be expressed graphically thus:



Gans measured the absorptive power of the zeolites by digesting them two days with Knop's solution of ammonium-chloride, and found that of the 120 mg. of the nitrogen contained in the solution there had been absorbed:

By the	Apophyllite	00.0 mg.
" "	Analcime	3.6 "
" "	Natrolite	29.1 "
" "	Zeolite Rümpler	30.0 "
" "	Desmine	42.0 "
" "	Stilbite	47.0 "
" "	Chabasite	69.0 "
" "	Artificial Zeolite of Gans	97.0 "

The above table shows that Rümpler's zeolites belong to the class of the aluminium double silicates owing to their inferior absorptive power.

Gans succeeded in manufacturing the so-called aluminate-silicates. He melted together three parts of kaolin, six parts of sand, and twelve parts of soda. The molecular composition of the resultant silicate is given by:

$$Al_2O_3 . 10SiO_2 . 10Na_2O.$$

From this point on, the development of zeolites has been rapid and the literature is too voluminous to permit of a complete summary in this discussion. There are something over 60 United States patents alone on the manufacture and use of natural and artificial zeolites.

A very interesting discussion of the various structural formulæ of the various zeolites is given by Asch and Asch.[7] They point out that in general hydroxyl groups attached to silicon are strongly basophillic (produce stable salts with metals), while hydroxyl groups attached to aluminum are weakly basophillic. This is in agreement with Gans' classification. (In the above formulæ and discussion only aluminum compounds have been mentioned. A parallel series of iron compounds is known which exhibits similar properties.)

Manufacture of Zeolites.

The composition and methods of manufacture of the artificial zeolite "Permutit" is given in Gans' patents[8] as follows:

> Among the great number of possible compositions of the melt the following two examples may be mentioned:
>
> 1. The following materials are mixed together, then melted and then extracted with water, viz.:

[7] *Silicates in Chemistry and Commerce*, Van Nostrand, 1919.
[8] U. S. Pats. 941,405, and 943,535.

Kaolin	3.0	parts by weight
Melted borax	2.4	" " "
Sodium carbonate	6.5	" " "

After extraction with water there remain behind undissolved crystalline zeolites having a strong faculty of exchanging their constituents.

The composition may be expressed by the formula

$$3SiO_2 . Al_2O_3 . Na_2O.$$

2. A mixture of:

Kaolin	2.5	parts by weight
Melted borax	1.5	" " "
Sodium carbonate	5.0	" " "

3. The following materials may be mixed together and then fused.

Kaolin	3	parts by weight
Quartz	6	" " "
Sodium carbonate	12	" " "

The molecular composition of this melt is as follows:

$$Al_2O_3 . 10SiO_2 . 10Na_2O.$$

The melt is subjected to extraction with water, thereby obtaining a crystalline alumino-silicate, which has the following composition:

SiO_2	= 46.0 per cent
Al_2O_3	= 22.0 " "
Na_2O	= 13.6 " "
H_2O	= 18.4 " "

The extraction of the melt with water has the effect of removing chiefly alkali-silicates, such as correspond to the formulæ:

$$Na_2SiO_3(K_2SiO_3) \text{ to } Na_4SiO_4(K_4SiO_4).$$

4. Or the following materials may be melted after mixing together:

Alumina	2	parts by weight
Quartz	12	" " "
Sodium carbonate	20	" " "

This melt has the same molecular composition and, on being extracted with water, it yields a product equal to that obtained from the melt according to the first example.

The products obtained by the present process are suitable chiefly for the purification or softening of water, also for the treatment of saccharine juices and molasses, to relieve them of the potash and soda which cause the formation of molasses, in order that large quantities of sugar may crystallize out of the liquid.

The purification or the softening of water may be effected in a simple manner by filtering the water through a layer of alumino-silicate containing sodium.

The chemical reaction may take place, for example, in the manner indicated by the following equation:

$$2SiO_2 . Al_2O_3Na_2O + CaH_2(CO_3)_2 = 2SiO_2 . Al_2O_3 . CaO + 2NaHCO_3.$$

Molasses and saccharine juices containing potash are filtered through alumino-silicates containing calcium, in which case the chemical reaction taking place may be expressed, for example, by the following equation:

$$2SiO_2 . Al_2O_3 . CaO + K_2O = 2SiO_2 . Al_2O_3K_2O + CaO.$$

Beside the fusion method mentioned above commercial zeolites are prepared by precipitation and by the processing of certain natural clays and sands.

One of the precipitation processes for the production of zeolite is described by Hilditch and Wheaton:[9]

> The base-exchanging compound, doucil, or sodium alumino-silicate, resulting from the interaction of a dilute solution of sodium silicate (containing 2-4 mols of silica to 1 of soda) and dilute sodium aluminate, washed, and dried (cf. E. P. 177,745; J. 1923, 372 A) conforms closely when anhydrous to Na_2O, Al_2O_3, $(SiO_2)_5$. In the manufacture, by careful adjustment of the concentrations of the aluminate and silicate solutions and of their respective soda contents and by suitable mixing devices, a perfectly homogeneous gel of the alumino-silicate is prepared; the gel is transferred with as little disturbance as possible to a dryer and slowly dried over a period of 4-5 days during which the water content is reduced from 90 to 50 percent: the hard gel, in the form of lumps of about 2-in. diam., is then washed in a slow stream of distilled water, subjected to further drying treatment for about one day and crushed to a convenient size. For use, material of ⅛-in. to 1/20-in. is the most suitable.

The natural zeolite glauconite or "greensand" has base-exchange properties but disintegrates in water especially when treated with strong salt solutions. To give the grains the necessary mechanical strength and resistance to disintegration the material is given a heat treatment. The temperature used is apparently just sufficient to cause superficial fusion or to glaze the surface of the grains. When properly treated "greensand" has much better physical properties than the synthetic zeolites although its exchange capacity is lower.

Certain clays exhibit base-exchange properties but for practical use they must be molded into grains and "baked" or "fired."

[9] *J. Soc. Chem. Ind.*, **43**, B 310.

Properties of Zeolites.

Applebaum [10] suggests the division of commercial zeolites into two classes: (1) *Porous zeolites.* This group includes the synthetic products. (2) *Non-porous or solid zeolites.* The treated green sands belong in this group.

These two classes differ with respect to the following five important properties.

a. Weight per cubic foot.
b. Amount of "bound water."
c. Total base exchange capacity.
d. Time to completely exhaust and to regenerate.
e. Salt required for regeneration.

A discussion of these properties is given by Applebaum as follows:

a. *Weight per cubic foot.* All zeolites have about the same specific gravity, 2.0 to 2.4. But the zeolites of the first group by reason of their porosity weigh less per cubic foot than the more solid zeolites of the second group. The various porous zeolites when in a moist condition weigh from 55 pounds or even less up to 70 pounds per cubic foot according to their porosity. They contain water up to 50 percent of the total weight. The non-porous zeolites in a moist condition weigh about 100 pounds per cubic foot and the amount of water contained is generally below 10 percent of the total weight.

The moisture content greatly affects the weight per unit of volume, but does not affect the volume itself. It is for that reason that purchasers should always insist on buying zeolite by volume rather than by weight. The writer's company very early in its career adopted the unit of volume rather than of weight in order to be fair to the consumer and to avoid misunderstandings which arise when zeolites are sold by weight and the moisture content varies during shipment.

b. *Water of hydration.* Zeolites are hydrous silicates, i.e., they contain water which cannot be driven off by heating them to a constant weight at 100° to 105° C. The water remaining at that temperature is often called water of hydration or water of constitution. The higher the amount of this residual water, the greater is the porosity of the zeolite and the greater the total exchange power of the zeolite.

c. *Base-exchange power between regenerations.* By this term is meant the total number of grains of hardness, usually expressed as

[10] *J. Am. Water Works Assoc.* 13, 213.

calcium carbonate, which a cubic foot of zeolite absorbs or exchanges up to the point when "zero-hardness" water is no longer produced. This may be called the "softening capacity" of the zeolite and must not be confused with the "total exchange" power. When the softened water first begins to come through the softener with a little hardness in it, it is time to regenerate. That is the practical end-point of a softener's run because the function of the zeolite softener is to produce nothing but "zero-hardness" water. But after this point is passed, the zeolite still has base-exchange power left and considerable additional water can pass through in a partially softened condition before the water emerges with the same hardness with which it entered.

The base-exchange power or water-softening capacity is directly proportionate to the active surface of the zeolite in contact with the water. Since the porous zeolites have an active interior as well as an exterior surface, it would naturally be expected to have greater water-softening capacity than the solid zeolites. The facts fulfill this expectation.

The softening capacity of a practically non-porous zeolite of about $\frac{1}{2}$ mm. grain size is about 2500 to 3000 grains expressed as calcium carbonate per cubic foot and with increasing porosity the capacity of the more porous zeolites increases to 10,000 grains expressed as calcium carbonate per cubic foot and higher. These figures are average values influenced to some extent by the water composition, the rate of softening and the amount of salt employed in regeneration, and the rate of regeneration. This means from the practical point of view that the amount of solid zeolites must be larger if they are expected to do the same work between regeneration as the porous ones.

d. *Rate of softening and rate of regeneration.* The higher water-softening capacity between regenerations of the porous zeolites can only be obtained by bringing the interior surfaces into action. The internal active surface of the porous grains are harder to reach than the external surfaces of the solid granules. The grain of a porous zeolite may be compared to a capillary tube, whereas the solid zeolite may be represented by a solid rod. In order to make contact with or sweep over the inner surface of the capillary tube it is necessary to displace the liquid contained within. It is well known that capillary tubes hold liquid by adhesion against the force of gravity and time must elapse before the contents are displaced. On the other hand, to pass the liquid over the external surfaces of the solid rod or the outside surfaces of the capillary tubes takes comparatively little time. This holds true with the water-softening reaction as well as the

reverse reaction of regeneration. Likewise it is possible to utilize quickly the outside surfaces only of porous zeolites.

Usually the time employed to exhaust a bed of zeolite is 6 to 12 hours, depending upon the convenience of the local plant and the length of the labor shift. It is possible to exhaust the water softener capacity of the zeolite bed in as low as two hours without decreasing its capacity but the greater amount of water used in washing and rinsing and the greater amount of labor required to regenerate the plant so frequently must be balanced against the lower cost of the smaller softener which a two hour run would permit.

During regeneration the brine must penetrate to the inner surfaces to bring out the calcium and magnesium previously removed and it takes more time and brine to do this than to brush by the external surfaces. Thus the solid zeolites and the outside surfaces of the porous zeolites can be regenerated in 20 to 30 minutes, whereas the interior surfaces of the porous zeolites may require one or more hours.

The porous zeolites are usually larger in grain size than the non-porous zeolites. This gives the latter somewhat more external surface area for the same volume of material. The smaller a sphere is the greater is the ratio of its surface area to its volume. But if the porous zeolites are reduced to the same grain size as the solid zeolite and only the external surfaces were called into action both types of zeolites will act at the same rate and produce that amount of soft water which corresponds to their exterior surfaces. The delay in bringing the liquid in contact with exterior surfaces causes the delay in utilizing them.

Thus all zeolites act instantaneously. It is not the stuff of which the solid zeolite is made or the way it is processed which makes it a "rapid-rate" material; it is merely the physical arrangement of the active reacting surfaces on the outside of the grain.

e. *Salt requirements.* Since, as explained above, the brine must overcome the adhesive power of the capillary passages of the porous zeolites, considerably more brine is used to accomplish a complete regeneration. If regenerated in the same way, the porous zeolites require about twice as much salt per kilogram removed, as the non-porous.

However, the brine that slips by unconsumed can be recovered and utilized again. This is the basis of the recovery method of regeneration which was invented several years ago.

With this recovery method the porous zeolites can be regenerated with the same net amount of salt as the non-porous, namely, about

one-half pound of salt per kilogram of hardness removed, expressed as calcium carbonate.

The Base-Exchange Reaction.

Baker [11] has pointed out that the rate of the base-exchange reaction is very high. The rate at which water may be passed through zeolite filters is dependent therefore on hydraulic rather than chemical limitations. He also found that with certain types of zeolites a water of zero hardness could not be produced from a raw water of over 30 grains per gallon hardness. The exchange capacity of porous zeolite is higher for calcium than for magnesium hardness but treated green sand removed calcium and magnesium equally well in Baker's experiments.

The base-exchange reaction simplified from Gans' statement above may be written

$$Na_2Z + CaX \leftrightarrows CaZ + Na_2X$$

where Z represents the zeolite radical and X is any diabasic acid. The usefulness of the zeolites naturally depends upon the reversibility of the reaction, as a result of which the sodium zeolite is reformed by treating the calcium zeolite with a strong solution of sodium salts.

Of the various investigations of the physical chemistry of the reaction may be mentioned those of Kornfeld,[12] Gunther-Schulze,[13] and Frankforter and Jensen.[14] Gunther-Schulze determined the ratio $\left(\frac{\text{Metal 2}}{\text{Metal 1}}\right)$ in permutit $: \left(\frac{\text{Metal 2}}{\text{Metal 1}}\right)$ in the solution, when sodium, ammonium, and potassium were used as Metal 2 (sodium permutit, ammonium permutit, and potassium permutit, respectively), and allowed to come to equilibrium with solutions of different concentrations of salts of calcium, barium, strontium, magnesium, silver and a large number of other metals (Metal 1). Table 15 gives the values found for some of the more important metals.

From the data in Table 15 Gunther-Schultze concluded that the greater the atomic weight the greater is the tendency of the metal to combine with the zeolite radical. This is in agreement with Frankforter's observation that in a mixture of calcium and barium salts, barium showed four and one-half times the replacing power of calcium.

[11] *J. Am. Water Works Assoc.* **11**, 128.
[12] *Z. Elektrochem.* **23**, 173 (1917); *Z. anorg. Chem.* **103**, 129; **108**, 215.
[13] *Z. Phys. Chem.* **89**, 168; *Z. anorg. Chem.* **116**, 16; *Z. Electrochem.* **28**, 85.
[14] *Ind. Eng. Chem.*, **16**, 621.

TABLE 15.—*Gunther-Schultze Ratio for Certain Metals.**

Metal 1	Metal 2	Ratio (Permutit calculated to 10 percent replacement)
Mg^{++}	NH_4^+	0.25
Ca^{++}	NH_4^+	3.00
Sr^{++}	NH_4^+	5.00
Ba^{++}	NH_4^+	50.00

* *Z. phys. Chem.* **103**, 129.

Character of Zeolite-Softened Water.

The most important characteristic of zeolite softened water is the practically complete removal of all calcium and magnesium ions. The amount of these ions remaining is so small that they cannot be detected by the soap test. The popular expression "zero hardness" is therefore justified in view of the definition of hardness given in *Standard Methods of the American Public Health Association.* By taking a large sample for analysis the writer has been able to detect small amounts of calcium and magnesium in zeolite treated waters, usually under 5 ppm., or 0.25 grain per gallon.

Since the softening reaction exchanges two sodium ions for each calcium or magnesium ion and since the atomic weight of sodium is more than half the atomic weight of calcium and nearly equal to the atomic weight of magnesium, there will be an increase in the total solids in the treated water. This is ordinarily not objectionable, except in some cases, for boiler feed.

Combination Treatment.

Since carbonate hardness may be removed by lime, which is cheaper than the corresponding salt requirement, waters are sometimes treated first with lime to remove the carbonate hardness and incidentally decrease the total solids, and then passed through a zeolite softener to remove the residual carbonate hardness and the non-carbonate hardness. In such installations it is necessary to add alum and filter after the lime treatment in order to prevent the incrustation of the zeolite granules.

Chapter IX.

Special Methods of Water Treatment.

Internal Treatment of Boiler Waters.

The activity of quacks and fakes in this field has led many chemists to conclude that there was no such thing as an internal boiler water treatment based on sound chemistry. The quack or fake treatments are characterized by certain easily recognizable earmarks.[1] In the first place they are advertised as cure-alls, guaranteed to remedy any condition with any water. In the second place they are recommended for use without any control or supervision, and thirdly, an analysis of the materials usually shows them to be either worthless and inert substances (cheap of course) or extremely dilute solutions of some of the commonly recognized scale preventives. In the latter case the customer is paying a fancy price for something that is 75 to 98 percent water. These characteristics are the same as those by which medical quackery may be recognized, and the "boiler compound" is analogous to a patent medicine. But just as there are plenty of reputable physicians, so are there competent chemical experts who can and do recommend certain well-established remedies for different types of boiler troubles.

Scale Prevention.

Internal treatment of boiler water involves the use of substances for the prevention of scale formation, foaming, and corrosion. Scale formation is prevented by inducing precipitation of calcium and magnesium under conditions such that the precipitate will form in a noncrystalline or amorphous condition in the body of the liquid and settle out as sludge which can be "blown off" instead of a crystalline deposit adhering to the heated surface. Two rather different types of reagents used separately or together tend to produce these results. One type is a reagent which forms compounds with the incrustants whose solubilities increase with rise in temperature so that precipitation will take place in the body of the liquid instead of at the slightly warmer

[1] French, *Ind. Eng. Chem.* 15, 1239.

metal surface. As pointed out in Chapter V, calcium sulfate decreases in solubility with temperature while calcium carbonate increases. If the carbonate-ion concentration is maintained at the proper value calcium carbonate will be formed as a sludge instead of calcium sulfate as a scale. The details of the control of this treatment are given by Hall: [1a]

To inhibit the formation of hard adherent scale on the evaporating surfaces, ionic concentrations in the boiler water must be so regulated that any solid phases in equilibrium are substances whose solubility increases with temperature increase. The growth of soft carbonate scale is controlled by imposing upon the feed water, either before or during its passage to the boiler, the conditions that its calcium salts shall rapidly reach equilibrium with the solid phase precipitating.

Generalized Conditions.—Let A_aB_b represent a salt of relatively low solubility, the slope of whose solubility curve dS/dT is positive, and let A_cD_d be one of the same order of solubility, but with dS/dT negative. At any temperature $T°$, at saturation,

$$[A]^a \text{ (ion)} \times [B]^b \text{ (ion)} = K \text{ sol. prod. } A_aB_b \text{ at } T°$$
$$[A]^c \text{ (ion)} \times [D]^d \text{ (ion)} = K \text{ sol. prod. } A_cD_d \text{ at } T°.$$

When conditions are so adjusted in a solution that it is in equilibrium with both solid phases, the value of A (ion) in both solubility product equations must be the same. Then

$$[B]^{\frac{b}{a}} \text{ (ion)} = \left(\frac{K^{\frac{1}{a}} \text{ sol. prod. } A_aB_b}{K^{\frac{1}{c}} \text{ sol. prod. } A_cD_d} \right)_{T°} \times [D]^{\frac{d}{c}} \text{ (ion)}.$$

In boiler operation, however, as evaporation occurs it is essential that the solid phase precipitation be one in which dS/dT is positive. This condition is fulfilled if at all times the concentration of B (ion) in the boiler water is maintained as follows:

$$[B]^{\frac{b}{a}} \text{ (ion)} > \left(\frac{K^{\frac{1}{a}} \text{ sol. prod. } A_aB_b}{K^{\frac{1}{c}} \text{ sol. prod. } A_cD_d} \right)_{T°} \times [D]^{\frac{d}{c}} \text{ (ion)}.$$

Note: If the B ion salt is one of extremely low solubility, the condition regarding the sign of dS/dT becomes of less significance. However, the presence of magnesium and calcium silicates in hard adherent scale in relatively large proportions is indicative of how small the solubility must be.

This inequality is the general criterion for preventing the growth of hard adherent scale on the evaporating surfaces.

[1a] *Ind. Eng. Chem.*, 17, 287, 409 (1925).

Specific Example of Adherent Scale Prevention.—As an example of its application in practical operation, we will show how calcium sulfate scale formation may be prevented by the use of soda ash as treating chemical, and how the decomposition of the carbonate ion at boiler temperatures minimizes magnesium silicate formation.

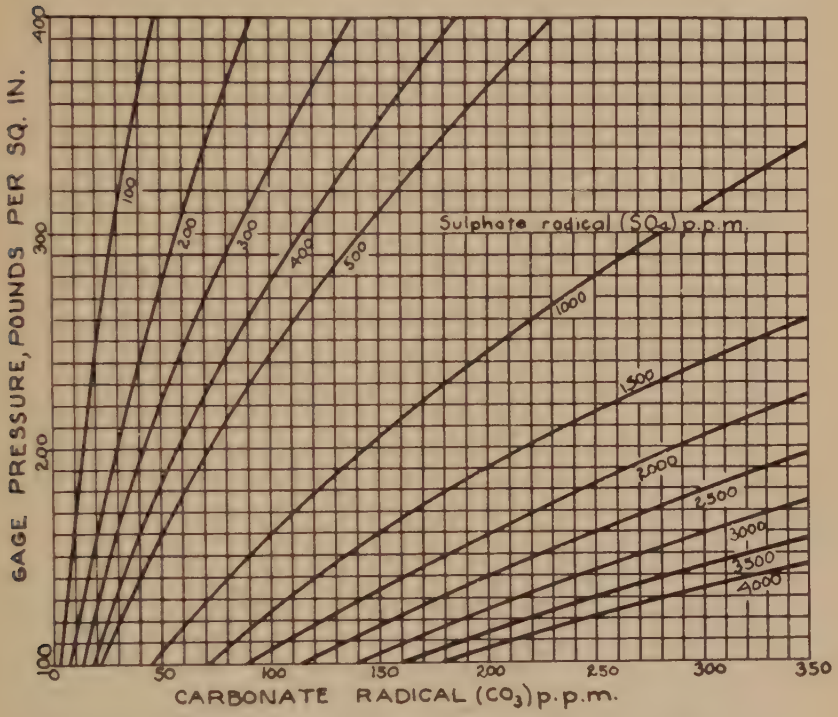


Fig. 16.—Relation of Carbonate Radical to Hard Scale (after Hall).

For this case the general inequality assumes the following form:

$$[CO_3^{--}] > \left(\frac{K \text{ sol. prod. } CaCO_3}{K \text{ sol. prod. } CaSO_4}\right)_{\substack{\text{Temperature of} \\ \text{boiler water}}} \times [SO_4^{--}].$$

(Also see Fig. 16.)

From the electrical conductivity of salts of the different ionic types Noyes and his co-workers [2] have determined their degree of dissociation over a wide temperature range. Since the ionization values for salts of any one ionic type are nearly the same,[3] the ionic concentration in saturated solutions of the sulfate and car-

[2] *Carnegie Inst. Pub.*, 63, 1907.
[3] Noyes and Falk, *J. Am. Chem. Soc.*, 34, 454 (1912).

bonate of calcium may be readily approximated from Noyes' data and their solubility products fixed for the range of temperature characteristic of boiler operation. Thus, at 185° C., K sol. prod. $CaSO_4 = 0.545$; and K sol. prod. $CaCO_3$. 0.077 (concentrations expressed in milliequivalents per 1000 grams of solution). Also, the degree of ionization of calcium sulfate and carbonate—salts of the same ionic type—by reason of application of the isohydric principle, is based upon the same total ionic concentration in the boiler water. This simplifies practical application by permitting the substitution of CO_3 and SO_4 determined analytically in place of CO_3^{--} and SO_4^{--}.

Finally the formation of adherent anhydrite scale on the evaporating surfaces of a boiler operating at 185° C. (150 pounds gage) is prevented by using soda ash to maintain the following condition in the boiler:

$$CO_3 \text{ ppm.} > 0.0883\ SO_4 \text{ ppm.}$$

The condition set up prevents formation of solid calcium sulfate in the boiler water, but deposition of hydrous magnesium silicate must also be controlled, else a hard adherent carbonate silicate scale may form if silicate is present in any quantity. It was under such conditions of no control that scales 7 and 8, Table 8 (page 85), were formed.

If the hydroxyl concentration in the boiler water is sufficient to depress the magnesium-ion concentration, however, the relatively small amounts of silicate in solution are insufficient to form magnesium silicate in troublesome quantity.

Fortunately, in the sense that it provides sufficient hydroxyl for this purpose, sodium carbonate in solution under boiler conditions readily decomposes into caustic soda and carbon dioxide. The elevated temperature is one factor in promoting the reaction: the low partial pressure of carbon dioxide in the rapidly regenerated gas phase is a second. For the extreme condition of a feed water exceedingly low in sulfate and high in magnesium, the decomposition of carbonate might not be sufficiently rapid to provide the essential hydroxyl concentration. In such a case the addition of hydroxyl as such would be necessary.

The second type of reagent for scale prevention includes various organic substances which apparently act as protective colloids.[4] Their action as explained in Chapter II is to prevent coalescence of the colloidal particles and to provide a solution link. The reagents most commonly used are the tannin extracts. Sugar, gelatin, cornmeal, starch and a wide variety of substances are also employed. In the presence of these substances precipitation is inhibited and when it does occur a soft sludge is usually formed instead of a hard adherent

[4] French, *loc. cit.*; Partridge, *Power*, **60**, No. 2; *see also* literature on protective colloids.

scale. These organic compounds are usually used together with soda ash or sodium hydroxide, which as mentioned above tend to prevent sulfate scale.

Foam Prevention.

For foam prevention or control it is apparently necessary to add some substance which will prevent the solid particles which stabilize the foam (Chap. V) from being drawn into the film. Castor oil appears to be very effective in that respect and certain crude mineral oils from the Southwestern States have been used with good results. It would appear that these oils coat the particles of suspended matter so that they are not wetted by the water and hence do not remain in the film. The organic substances used to inhibit scale formation are reported to have a beneficial effect on foaming. This may be due to the formation of flocculent rather than granular particles which are not suitable for foam stabilization.

Of the mechanical means for preventing foaming, "blowing down" the boiler is the most generally used and in fact it is recommended no matter what treatment is given the boiler water (except of course distillation). The blow-down schedule will have to be determined on the basis of the composition of the feed water, the rate of evaporation and the maximum concentration under which the boiler will operate. In some cases the blow down is practically continuous, while in others it may be once or twice a week or even less frequent. A continuous filtration of the water from the boiler without reduction in temperature is recommended by Hall and co-workers[5] and a centrifugal purifier for removing moisture and soluble salts from the steam is also recommended by these authors. The Hotchkiss skimming apparatus[6] is another mechanical device for removing turbidity from the boiler.

Barium salts, especially the hydroxide, have certain chemical properties that recommend them. The fact that both barium carbonate and barium sulfate are very insoluble makes it possible to treat both carbonates and sulfates with barium hydroxide:

$$CaSO_4 + Ba(OH)_2 \rightleftarrows Ca(OH)_2 + \underline{BaSO_4} \qquad (1)$$

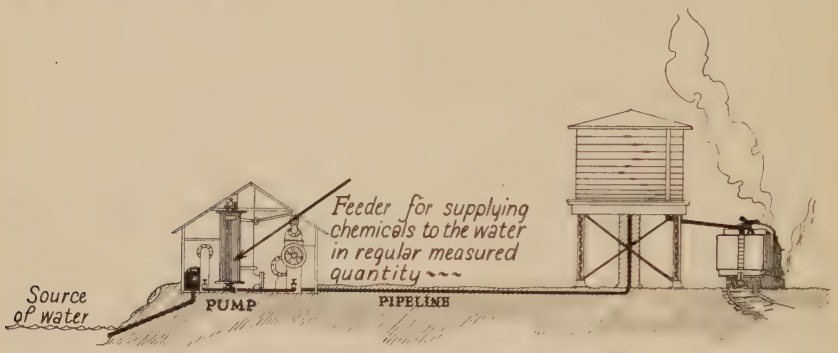
$$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftarrows \underline{2CaCO_3} + 2H_2O. \qquad (2)$$

The fact that barium hydroxide is expensive and rather poisonous has apparently limited its use.

[5] *Iron Steel Eng.*, **1**, 312 (1924).
[6] Booth, *Water Softening and Treatment*, p. 119.

Prevention of Corrosion by Internal Treatment.

For the prevention of corrosion by internal treatment sodium silicate (water glass) is extensively used. It forms a thin firm scale or coating which protects the boiler tubes from corrosive action. The alkaline



(*Courtesy Paige & Jones Chemical Co.*)

FIG. 17.—Wayside Tank Treatment.

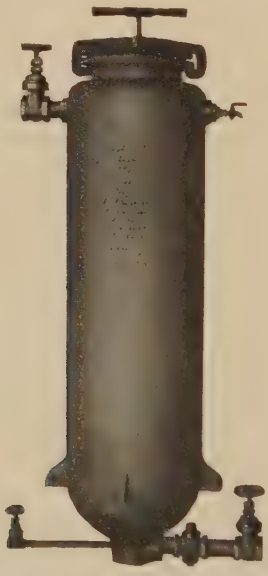


FIG. 17a.—Feeder for Supplying Chemicals to Water in Regular Measured Quantity.

treatment used for scale prevention usually raises the pH to a point where corrosion is considerably inhibited (*see* Fig. 8, p. 97). Granular zinc or iron or zinc or iron plates are sometimes introduced into a

boiler to allow corrosion to take place on them rather than on the boiler metal.

Three formulæ for prevention of corrosion have been patented by Speller:[7]

1. A deoxidizing and neutralizing boiler composition which also forms a protective coat on the metal is prepared by mixing concentrated solutions (15 percent) of sodium silicate and sodium sulfite in about equal proportions.

2. Granular ferrous sulfate and granular caustic soda are intimately mixed by grinding. The thick mortar formed, which is composed principally of ferrous hydroxide is shaped into briquettes and allowed to set.

3. A ferrous hydroxide composition is obtained by intimately mixing granular ferrous sulfate and a granular alkaline compound, e.g., hydrated lime, and subjecting the mixture to a pressure of not less than 2000 lb. per sq. in.

Control of Internal Treatment.

The control of the addition of reagents for internal treatment of boiler water is often haphazard and dependent upon the whims of the boiler room crew. Too often the principle that "if a little is good, a good deal is better" is the basis of the treatment. Good results cannot be expected under such conditions. The method of introducing the chemicals will depend upon the feed water connections. In railroad work the water may be dosed in the tender by a trained attendant or the water may be dosed as it is pumped into the wayside tank. For the latter type of treatment the formula contains enough protective colloidal material to prevent precipitation until the water is heated.

Prevention of Corrosion.

Protective Coatings.

There are naturally two general methods of preventing corrosion: the metal may be given a corrosion-resisting coating, or the corrosive agent or agents may be removed or neutralized. A large number of materials have been used to coat and protect the mains and house connections of water supply systems, many of them with good success. Among them asphalt, cement, and the various metal coatings, especially zinc, have been the more popular. The question of protective coatings lies outside the field of water treatment but mention may be made in

[7] U. S. Pats. Nos. 1,531,989-91 and 1,531,993.

passing of the two most important requirements for successful protection. First, the metal surface must be absolutely clean to provide bonding contact for the coating, and second, the coating material must cover the metal and dry or set without shrinkage so that there will be no pinholes. An imperfectly applied coating may result in worse corrosion than bare metal.

The slow precipitation of calcium carbonate in distribution mains as the result of the use of unfiltered softened water has already been discussed. The remedy was found to be carbonation to such an extent that the water will contain a small amount of carbon dioxide in excess of that required to prevent the precipitation of calcium carbonate. In the case of corrosive waters it may be advantageous to have a thin incrustation of the lime precipitate as a protection to the distribution system. This can easily be accomplished in the case of a softened water by proper regulation of the carbonation. In the case of a naturally soft water high in carbon dioxide the same result could be obtained by adding calcium hydroxide. If this type of treatment is alternated with periods during which a small amount of aggressive carbon dioxide is permitted in the system it should be possible to steer a course between corrosion and objectionable incrustation. This protection does not depend on raising the pH to avoid corrosion since in this range pH has very little effect on corrosion. It is a case of increasing the calcium-ion concentration and the carbonate-ion concentration so that their product will exceed the solubility product constant for calcium carbonate.

In connection with internal treatment of boiler water mention was made of the use of sodium silicate to prevent corrosion, and its usefulness in this respect was attributed to the formation of a coating on the metal surface. The same treatment is favored by Speller [8] for hot water systems where the line of travel is not over 200 feet from the point application. A treatment to give 15 to 30 ppm. increase in alkalinity is recommended at first, with a later reduction to 5 to 10.

Thresh [9] recommends sodium silicate (10 ppm.) for treatment of municipal systems and reports that relief from "red water" occurred within two to three days after the commencement of treatment. The precipitate is not formed so quickly in the cold and hence is distributed throughout the system.

Baylis [10] has called attention to the protective action of the coat-

[8] *Corrosion*, McGraw-Hill, 1926.
[9] *Examination of Waters*, 3rd ed., pp. 78 and 133.
[10] *Ind. Eng. Chem.* **18**, 370.

ing formed by the first products of corrosion, namely, ferrous hydroxide and ferrous carbonate. Beside having a mechanical protecting effect, these compounds act as buffers, raising the pH next to the metal.

The chromates or dichromates are sometimes used in boiler compounds and in industrial plants to prevent corrosion of iron. They are said to render the iron "passive" or inert. They should be used with caution since in some cases their use has apparently aggravated conditions rather than remedied them.

Elimination of Corroding Agents.

Whatever may be the secondary factors influencing corrosion the two basic factors are oxygen concentration and hydrogen-ion concentration. In most natural waters the hydrogen-ion concentration falls in the "neutral zone" where it has relatively little effect. In the case of acid waters the addition of alkali to raise the pH to the neutral zone is comparatively simple. Raising the pH to the "alkaline zone" is not ordinarily worth while for the prevention of corrosion. Lime softening incidentally leaves a water in the latter zone.

Removal of Oxygen. The removal of oxygen, when conditions are such that it can be accomplished, comes nearer to completely preventing corrosion than any other one treatment. There are two methods by which oxygen may be removed: (*1*) raising the temperature or decreasing the pressure both of which decrease the solubility of the oxygen; and (*2*) treatment of the water with some reducing agent. A combination of the two processes may be advisable. The first process is ordinarily referred to as *deaëration* and the second as *deactivation.* There are a good many forms of apparatus designed to carry out either deaëration or deactivation or both together. They have been discussed at some length by Speller.[11] Figure 18 by Speller serves to illustrate the principle involved. The minimum oxygen allowable is reported to be from 0.05 to 1 cc. per liter. Deaërators operating at 25 inches of mercury (vacuum) and 65° F. reduce the oxygen to 1 cc. per liter. The removal of carbon dioxide by deaëration was found by Jackson & McDermet [12] to raise the pH by 2.5. In deactivators iron scrap of some sort is usually employed although other metals and reducing agents may be used. The use of iron necessitates a pH of 9 or more to precipitate the iron dissolved in the deactivator. The amount of iron consumed in a year is given by Speller as 40 pounds per thousand gallons per hour, per cubic centimeter of oxygen per liter.

[11] *Loc. cit.*
[12] *Ind. and Eng. Chem.* **15**, 959.

Iron Removal.

In the majority of cases iron appears to exist in water as the ferrous salt, probably the bicarbonate. As mentioned above it is removed along with calcium and magnesium in water softening. When the water is not to be softened the usual process is aëration and filtration.

Aëration introduces oxygen into the water causing the oxidation of ferrous ion to ferric ion. At the same time carbon dioxide is released

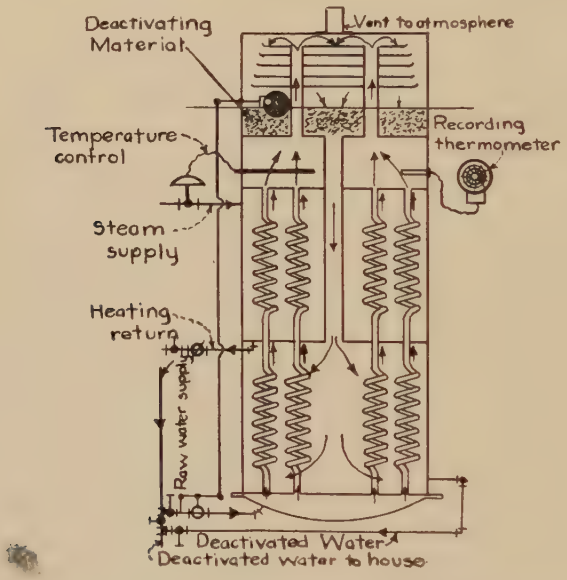


FIG. 18.—Mechanical Water Deaërator.

In operation the cold water enters the aërator at the bottom and flows upward through the coils, taking up some heat from the down-flowing water. The temperature of the water is raised to about 205° F. (96° C.) as it passes through the middle steam-heated compartment. From this the water rises and flows over baffles, where the air is nearly all separated, the residual oxygen being removed by some suitable deactivating material before the water passes downward to the outlet, its temperature being reduced to about 150° F. (66° C.) in passing through the lower heat exchanger.

raising the pH and favoring the precipitation of the basic carbonate or oxide. (Most well waters are supersaturated with CO_2 when brought to the surface.) Sedimentation after aëration removes but a small portion of the iron except in very heavily laden waters. This is due to the formation of a rather stable sol. Aërated iron-bearing water has a distinctly opalescent appearance that persists for 12 to 24 hours without the formation of much precipitate. Filtration assists in the coagulation

of this sol as it does in the removal of the final portions of alumina (*see* Chap. X).

Weston [13] described some interesting experiments with iron removal and presented a theory of the mechanism of the reactions:

> Iron-bearing ground waters are present in three classes: (1) those beginning to precipitate immediately after aëration, (2) those in which iron is not easily precipitated by aëration (acid waters), (3) those which precipitate part of the iron readily but hold the remainder indefinitely (waters carrying also organic humus material).
>
> The water supply studied is obtained from an infiltration gallery located in sand and gravel along the bank of the Ipswich River. The surface soil above the gallery is a black muck. At times when the river is high there is considerable seepage through this muck and at such times the color of the water is exceedingly high. When the water contains considerable amounts of this organic matter from the seepage water, the iron is exceedingly hard to remove. This may probably be due to the fact that the organic matter acts as a protective colloid to the iron. When there is considerable amount of this seepage material, boiling the water increases the color by 30 percent and does not cause precipitation of the iron as would be expected. Furthermore, after boiling it is almost impossible to remove the iron. Apparently boiling facilitates the combination, whatever it may be, of the organic matter with the iron. Treatment with carbon dioxide seems to inhibit the combination of organic matter with iron, making the iron more easily removed.
>
> Various attempts were made by the Massachusetts State Board of Health and other chemists to solve this difficult problem but without marked success. The most feasible system appeared to be the treatment with lime which precipitates the organic matter. Alumina was also used, the amounts being 3 grains per gallon of alum and about a half grain per gallon of lime (150 lbs. to 200,000 gallons). In 1908 the author suggested that colloidal clay being negative and colloidal iron being positive the treatment with clay should facilitate the removal of iron. Furthermore it is well known that when a highly colored river empties into a very turbid river the color is largely adsorbed on the sustained turbidity so that the resultant water after sedimentation carries very little color. It is also known that positively charged aluminum ions are effective in precipitating negative suspensoids. In view of these considerations the author added colloidal clay to the water at Reading and then alumina to remove the excess clay. The results on the experimental scale were very satisfactory so that the use of clay and alum was substituted for the use of lime and alum and the amount of lime used reduced to 15 pounds per 200,000 gallons of water and one grain per gallon of alum. This system had been in operation from April 19, 1908, until the date of the article giving uniformly good results.

[13] *Proc. Am. Soc. Civil Eng.* **34**, 1324.

Another advantage of changing from lime to clay in this particular instance was that the addition of lime increased the hardness of the water, the raw water being exceptionally soft.

The use of lime is apparently a disadvantage unless the water is to be softened, except in the case of acid waters. The slimy nature of the iron deposits often matted with the growth of "iron bacteria" makes the maintenance of the filter more difficult.

Removal of Manganese. The process for the removal of manganese is similar to that for the removal of iron. It is necessary to have the sand grains coated with manganese dioxide before any removal takes place.[14] The use of "permanganate permutit" (zeolite treated with $KMnO_4$) for removal of manganese has been found successful, probably due to a coating of manganese dioxide on the grains.

[14] Corson, *Ill. State Water Survey Bull.* 13, p. 178, and references cited by Corson.

Chapter X.

Water for Domestic Use.

Specifications.

Water for domestic use must be free from infection of all sorts. This requirement is of fundamental importance but mere disinfection is accomplished with such comparative ease by the addition of chlorine that it is one of the less troublesome chemical problems of water treatment. A discussion of bacterial standards belongs to the subject of bacteriological water analysis rather than here. Statistics indicate that a water which does not carry on an average more of the colon group of intestinal organisms (B. coli) than 2 per 100 cc. is safe.[1]

Physically, water should be as clear and colorless as possible. It should have no pronounced taste nor odor and its temperature should preferably be low. A turbidity of ten parts per million on the silica scale is ordinarily noticeable in a drinking glass and a color of 10 on the platinum scale can be detected under similar conditions. No quantitative limits of tastes and odors have been adopted. The production of a water which will satisfy these physical requirements involves many important and difficult chemical problems.

A general view of the water production industry is given in the following extract from an article entitled "Water Works Statistics" appearing in *Public Works*, May 1923, **54**, 174.

> The water purification data compiled were given in reply to these questions: "In treating your water do you use sedimentation basins?" "Filters?" "What kind of filters?" "Do you chlorinate it?" "Do you soften it?" "Do you treat it in any other way?" "What was the cost of the purification plant?" "How many gallons were treated last year?" "What was the cost last year for labor at purification plant?" "What was the cost of chemicals?" "What was the cost of repairs?" "What was the cost of power?" "What were other costs of purification?" Replies were received from over 600 water works.
>
> We have summarized the information concerning the methods of treatment employed by the various cities with the following results:

[1] For a complete discussion of sanitary standards see *U. S. Pub. Health Rept. 40, 693.*

Of all the plants reporting, 26.6 percent treat the water in sedimentation basins; 26.9 percent treat it in filters, 1.8 per cent of these being pressure filters, 2.4 per cent slow sand filters and 22.6 per cent rapid sand filters. Five cities reported infiltration galleries, and two reported natural filters (sand or gravel in place); 41.6 per cent of the plants reported chlorinating the water, four of them treating part of the water only in this way and nine of them only part of the time. Twenty-four plants reported softening the water, twelve used copper sulfate, four aërated, one used an iron removal process and one the excess lime process.

The quantity of water should be adequate for the needs of the city. These vary widely with the customs and habits of the people and the character of the community. In Europe 20 to 50 gallons per capita per day are required, while in America 75 to 150 gallons per capita per day may be consumed. The amount used for actual human consumption including cooking is but a small fraction of the total (5 percent in some cases), the bulk of the supply being required for industrial uses, flushing away wastes, etc. Where the total consumption is 125 gallons per capita per day, 50 gallons will probably be used by industries, 40 gallons for domestic use, 10 gallons for municipal purposes and 25 gallons will be unavoidably wasted.

Well Supplies.

With the exception of softening and iron and manganese removal, which are treated in a separate section, there is little chemistry involved in the production of potable water from wells. In general wells for large supplies are so located that the water obtained is not bacterially polluted and most well waters are clear and colorless. If the well is properly constructed and the top is protected by a suitable curbing no treatment is required except perhaps where the softening, etc., is desirable. Where wells have been poorly located or constructed or where a considerable population has grown up around the well sites they may be subject to pollution. In such cases disinfection as with chlorine is all that is required.

Surface Supplies.

Collection.

The first step in any chemical manufacturing industry is to secure the raw material. Surface water may be taken directly from rivers if the flow is sufficient or from lakes. In some cases, as in ancient Rome, or modern New York or San Francisco water has been transported in

aqueducts for many miles when suitable supply was not available nearby. Frequently artificial lakes or reservoirs are constructed to collect the rainfall which would ordinarily run off and hold it for use during times of low precipitation. In some arid regions communities are forced to depend on huge cisterns. This is true at Jerusalem in Palestine.

Treatment.

Reservoir Control. The first step in the treatment of surface water supplies is the protection of the watershed from pollution. Sometimes this can be applied to a high degree as it is in the case of the New York City supply. When the water is collected from an extensive area complete removal of all sources of pollution would be too expensive and impractical and supervision must be limited to the reservoir only. Watershed control is a question of hygiene and public health rather than of chemistry and will be found adequately treated in standard works on preventive medicine, public health, etc.

A reservoir or lake usually provides a suitable environment for the growth of microscopic plants and animals (algae and protozoa) all of which increase the organic content of the water and many of which produce characteristic essential oils which cause tastes and odors in the water. Microscopic examinations from time to time will reveal the character and extent of these growths. They are best controlled by the addition of copper sulfate applied by dragging the chemical around the reservoir in a sack at the stern of a boat until it is dissolved. The amounts required to kill different organisms are given in the accompanying table from *Water Works Practice Manual* of the Am. Water Works Association.

It was formerly supposed that the copper ions were partially adsorbed by organisms to which they are toxic and partially precipitated as the basic carbonate. Hale and Muer, however, have recently reported data [2] which indicate that all of the copper is found deposited on the iron pipes of the distribution system. No cases of human poisoning by copper as a result of this treatment have been reported. Fish are frequently killed unless the copper sulfate is applied so as to avoid high local concentrations. Application to the ice shortly before it melts in the spring has been suggested [3] as an effective means of securing even distribution and Rushton and Aubion [4] used an ordinary agri-

[2] *Eng. Contr.* **64**, 66.
[3] Revis, *Eng. News-Rec.* **94**, 660.
[4] *Eng. Contr.* **63**, 125.

TABLE 16.—*Copper Sulfate Required for Treatment of Different Genera.*[1]

Organisms	Odor	Parts per Million	Pounds per Million Gallons
Diatomaceae:			
Asterionella †	Aromatic, geranium, fishy	0.12*-0.20*	1.0-1.7
Cyclotella †‡	Faintly aromatic		
Diatoma ‡	Faintly aromatic		
Fragilaria ‡		0.25	2.1
Melosira †‡		0.33	2.8
Meridion	Aromatic		
Navicula ‡		0.07	0.6
Stephanodiscus		0.33	2.8
Synedra ‡	Earthy	0.50*	4.2
Tabellaria †	Aromatic, geranium, fishy	0.12*-0.50*	1.0-4.2
Chlorophyceae:			
Cladophora ‡		0.50	4.2
Closterium		0.17	1.4
Coelastrum ‡		0.05-0.33	0.4-2.8
Conferva ‡		0.25	2.1
Desmidium		2.00	16.6
Dictyosphaerium †	Grassy, nasturtium, fishy		
Draparnaldia		0.33	2.8
Entomophora		0.50	4.2
Eudorina	Faintly fishy	10.00	83.0
Hydrodictyon		0.10	0.8
Microspora		0.40	3.3
Palmella		2.00	16.6
Pandorina	Faintly fishy	10.00	83.0
Raphidium		1.00	8.3
Scenedesmus		1.00*	8.3
Spirogyra ‡		0.12	1.0
Staurastrum		1.50	12.5
Ulothrix		0.20*	1.7
Volvox	Fishy	0.25	2.1
Zygnema		0.50	4.2
Cyanophyceae:			
Anabaena †	Moldy, grassy, nasturtium, vile	0.12*	1.0
Aphanizomenon †	Moldy, grassy, nasturtium, vile	0.12*-0.50*	1.0-4.2
Clathrocystis	Sweet grassy, vile	0.12*-0.25*	1.0-2.1
Coelosphaerium †	Sweet grassy	0.20*-0.33	1.7-2.8
Cylindrospermum	Grassy		
Microcystis		0.20	1.7
Oscillaria ‡		0.20-0.50*	1.7-4.2
Rivularia	Moldy, grassy		
Protozoa:			
Bursaria	Irish moss, salt marsh, fishy		
Ceratium	Vile stench (rusty brown color)	0.33	2.8
Chlamydomonas		0.50	4.2
Cryptomonas	Candied violets	0.50	4.2
Dinobryon	Aromatic, violets, fishy	0.25*	2.1
Euglena		0.50	4.2

TABLE 16 (*Continued*)

Organisms	Odor	Parts per Million	Pounds per Million Gallons
Protozoa (*Continued*)			
Glenodinium	Fishy	0.50*	4.2
Mallomonas	Aromatic, violets, fishy	0.50	4.2
Peridinium	Fishy, like clam-shells	0.50*-2.00	4.2-16.6
Synura †	Cucumber, muskmelon, fishy, bitter	0.12*-0.25*	1.0-2.1
Uroglena †	Fishy, oily, cod liver oil	0.05*-0.20*	0.4-1.6
Schizomycetes:			
Beggiatoa ‡		5.00	41.5
Cladothrix		0.20	1.7
Crenothrix †‡		0.33	2.8
Leptothrix ‡			
Fungus:			
Leptomitus		0.40	3.3
Miscellaneous:			
Chara ‡		0.10-0.50	0.8-4.2

[1] *Water Work Practice,* pp. 168-9.

The organisms where odors are expressed have been in sufficient quantity in water supply at one time or another to cause the characteristic odor.

* Dosage successful in New York City's supplies.

† These organisms have been affected by chlorine and in some cases controlled by dosage ranging from 0.5 to 2 ppm. depending largely on amount of organism.

‡ These organisms have caused trouble other than odor.

cultural spraying machine applying a dose of 0.05 ppm. on three successive days to give a total dose of 0.15 ppm.

Since the algae are dependent upon carbon dioxide for the production of their food by photosynthesis, V. gobinda Raju [5] has suggested the use of lime to arrest their growth. This was found unsuccessful. But the addition of sulfuric acid to completely neutralize the alkalinity was found effective. Raju assumes that this treatment drives out all the carbon dioxide. It should be noted that this treatment would produce a pH which can be tolerated by only a few forms of plant life.

Stratification and Overturning. The fact that water has its greatest density at a temperature somewhat above its freezing point and that wind and wave action does not ordinarily extend to a depth greater than 50 feet especially when difference in density of the water offers a resistance to such action, give rise to a seasonal cycle of changes in deep lakes and reservoirs which has an important effect on the quality of the water drawn from them.

[5] *Indian J. of Med. Research,* **11,** 1057.

If we were to examine the temperature of a lake in the temperate zone in mid-winter it would be found to be 0° C. just under the ice. As the thermophone or thermocouple is lowered the temperature will be found to rise gradually to a little less than 4°. The water at 0° is less dense than that at 4°, hence it will remain at the top. This is known as "inverse stratification," since the colder water is on top. When the ice melts and the weather becomes warmer in the spring the temperature will gradually rise until it is 4° at the top and hence heavier than at the bottom and the surface water will sink. At this time there is no difference in density to offer a resistance to wind action and the result is that the first spring storm will cause a "spring overturning" or a complete mixing of the waters of the lake. The entrance of slightly warmer ground water through springs in the bottom will aid this overturning.

As the surface water continues to become warmer with the advancing summer it will then remain on top except as it is stirred under by wind and wave. By July we would find the temperature in the upper 30 to 40 feet ranging perhaps from 20° C. at the top to 12° to 14° at a 30 to 40 foot depth, but in the next 5 to 10 feet the temperature will drop abruptly and then more gradually reach a temperature a little above 4° at the bottom. This zone in which the temperature drops sharply is called the thermocline and marks the depth to which wind action has been felt. This difference in temperature also represents a corresponding difference in density with a resulting stratification, the "direct" or summer stratification.

Then as the surface cools in the fall the cooler water sinks to the level of the thermocline until the temperature reaches 4° at the top, while at the bottom it is a little warmer and hence lighter. This difference in density aided by wind action causes the "fall overturning." As the cooling continues and the ice sheet is formed the "inverse" or "winter stratification" occurs and the cycle is complete. This cycle will naturally vary with the climate and the depth of the lake. In shallow lakes there will be no summer stratification; wind and wave action prevent it.

Naturally these periods of stratification and overturning will affect the chemical content of the water and especially the amounts of free carbon dioxide and oxygen at different levels and at different times.

There is also an interesting relation between these two gases and the plant and animal life in the lake which in turn follows the temperature changes just discussed. Living cells use up oxygen and give off carbon dioxide as a waste product so that in the portion of a stratified

lake below the thermocline where there is no chance for a gain of oxygen from the circulation of surface water and no exposure to the surface to liberate the excess of carbon dioxide the oxygen content will drop to a very low figure and the carbon dioxide will rise correspondingly.

Green plants at the same time are capable of taking up carbon dioxide and liberating oxygen during the time that they are exposed to

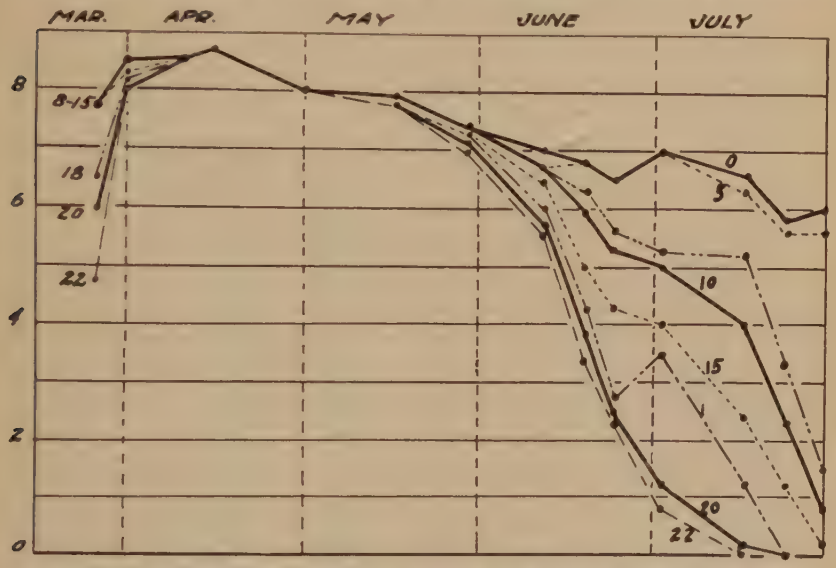


FIG. 19.—Variation of Dissolved Oxygen with Depth and Season (Wis. Geological and Natural History Survey Bull. No. 22).

light, by the well recognized process of photosynthesis. Although there must be intermediate steps in the process the reaction may be summed up by the equation $CO_2 + H_2O \leftrightarrows (C_6H_{10}O_5)_n + O_2$. In many lakes a large enough number of microscopic green plants (algae) are found free floating to use up a considerable amount of carbon dioxide and liberate a proportionate quantity of oxygen. The consumption of carbon dioxide will displace the reaction

$$Ca(HCO_3)_2 \rightleftarrows CaCO_3 + H_2O + CO_2$$

to the right resulting in an increase of the pH to from 8 to 9 and in some cases enough calcium carbonate may be formed to produce a precipitate. The presence of the normal carbonate ($CaCO_3$) will be shown by a "phenolphthalein alkalinity" which is sometimes called "negative CO_2."

Pure oxygen is roughly five times as soluble as oxygen diluted with nitrogen as it is in the air. When the oxygen is being liberated by photosynthetic action more rapidly than it can come to equilibrium with the air at the surface it is found by analysis in "supersaturated" amounts. The depth at which this photosynthesis may take place will depend on how far sufficient light can penetrate the water. In some cases this may be as much as 30 feet.

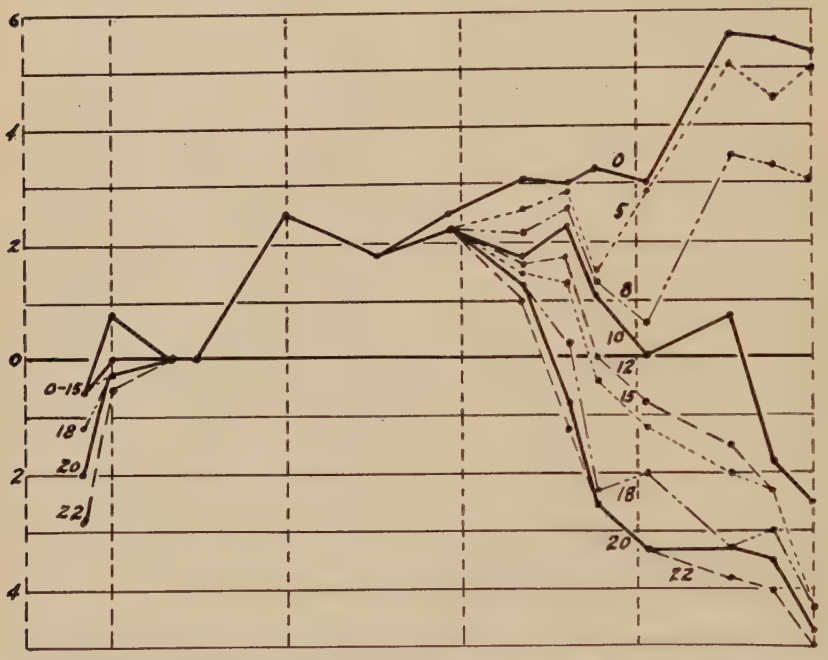


FIG. 20.—Variation of Carbon Dioxide with Depth and Season (Wis. Geological and Natural History Survey Bull. No. 22, page 43).

The change of carbon dioxide and oxygen content with depth and with the season is well illustrated in the accompanying diagrams from Bulletin 22 of the State Natural History Survey of Wisconsin by Birge and Juday. The observations begin shortly before the spring overturning and extend through to the establishment of the summer stratification.

Water which is cool is more palatable, and tastes and odors are not noticeable. In the case of deep reservoirs where summer stratification occurs temperature studies for the location of the thermocline should be made and the intake placed where it will draw a cool water.

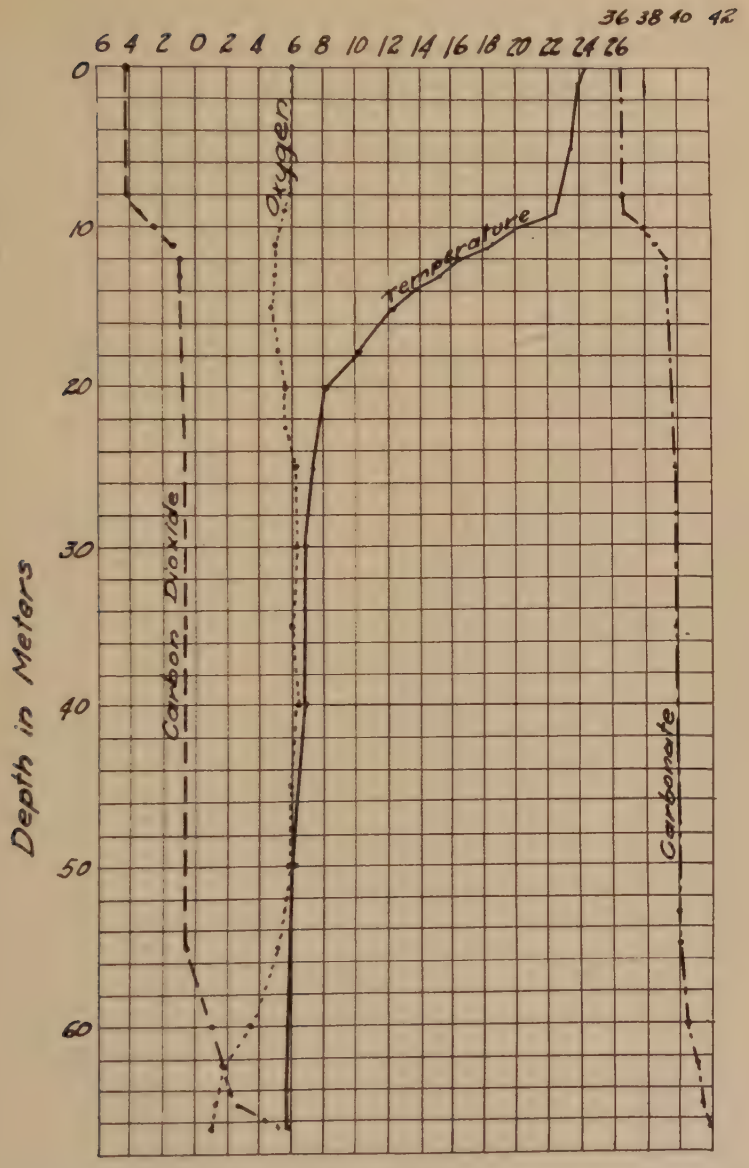


FIG. 21.—Summer Stratification (Wis. Geological and Natural History Survey Bull. No. 22, page 43).

Other Effects of Storage. While the reservoir is primarily designed to provide storage for the necessary quantity of water, it is at the same time an important part of the purification equipment. The coarser suspended matter settles out and if the time of storage is considerable, pathogenic bacteria will die off. The effect upon the turbidity is especially noticeable at times of heavy run-off when large amounts of silt are carried into the reservoir. The peak load on the filters at such times is much less than it would be without the reservoir. Records at various water works indicate a decrease in the required coagulant with the installation or enlargement of a reservoir.

The effect of storage on bacteria has been extensively studied by Sir Alexander Houston and his results will be found in his reports to the Metropolitan Water Board (London). From five to seven days storage was found to result in better than a 99 percent reduction in typhoid organisms.

It has also been reported [6] that storage reduced the color of the water, due apparently to a bleaching action of the sunlight.

Where a water supply is taken directly from a turbid river it is frequently advantageous to provide preliminary settling basins. At Omaha, Neb.,[7] where the Missouri River frequently carries 2500 parts per million of sediment, mud will accumulate in the sedimentation basins to a depth of several feet in 24 hours.

Storage in reservoirs or plain sedimentation is not sufficient to remove all impurities. Only the coarser suspended matter will settle out. If there is clay or other material which is colloidal it will remain in suspension. This may amount to 200 parts per million or more in many cases.

Coagulation and Filtration. To remove the non-settleable impurities, both turbidity and color, two further steps in the treatment are usually employed, namely, coagulation and filtration. In some plants of an earlier design filtration alone is employed at a slow rate.

Coagulation is accomplished by adding to the water a salt, usually the sulfate of aluminum or iron, which hydrolyzes forming the flocculent hydroxide. When the alkalinity of the water is not sufficient to cause complete hydrolysis it is sometimes necessary to add lime or on the other hand results are sometimes better if acid is added.

Coagulation Equipment. The process of coagulation is ordinarily carried out in large concrete basins frequently divided into compartments by walls. The first compartment is constructed to cause thorough

[6] Saville, *J. New Eng. Water Works Assoc.*, **39**, 145.
[7] Leisen, *Eng. News-Rec.*, **92**, 925.

mixing of the chemical with the water. This is accomplished in a variety of ways; baffles, jets, jumps, paddle wheels, etc., are used. The rest of the basin is mainly required to permit the bulk of the floc and impurities to settle. Appropriate feeding devices are required to proportion the dose of chemicals to the flow of water.

The work accomplished by sedimentation and coagulation is seen in the current report [8] of the Water Commissioner of St. Louis, Mo., which shows that in the year ending April 13, 1925, 43,992.12 million gallons were pumped in the low service system, and that the following matter was removed from it:

Suspended matter	246,512	tons
*Dissolved matter	17,720	"
Coagulants precipitated	33,099	"
Total	297,331	tons

* Partial softening is employed.

This total was more than 150,000 tons less than for the preceding year, when the largest amount on record was removed. Of the solids removed in the year covered by the report 31,497 tons, or 13 percent of the total, was removed by the grit chamber.

The time actually allowed for coagulation varies from a few seconds in the case of pressure filters to 24 hours or more. The time required for good coagulation varies greatly with different waters. In most cases it is found that a coagulation period of less than 4 to 6 hours leaves an unfair portion of the work to be done by the filters.

The mixing previous to settling has a considerable effect on the time required in the coagulation basin. Hoover [9] has shown that 20 minutes mixing at a velocity of 0.6 foot per second and one hour settling gave better results than six hours quiescent settling. Some plants which are required to treat a variable water find an experimental laboratory mixer useful for routine plant control.

[8] Removal of Dissolved and Suspended Matter from St. Louis Water, *Eng. Contr.* (*Water Works Issue*), **64**, 357 (1925).
[9] *J. Am. Water Works Assoc.* **11**, 582.

Chapter XI.

Chemistry of Coagulation.

Ionization of Aluminum Hydroxide.

Attention has been called (p. 29) to the fact that aluminum hydroxide is an amphoteric substance, that is, it acts both as a base and as an acid. It may ionize in two ways

$$\frac{Al(OH)_3}{(Precipitate)} \begin{cases} \swarrow Al(OH)_2O^- + H^+ & \textbf{(A)} \\ \searrow Al(OH)_2^+ + OH^- & \textbf{(B)} \end{cases}$$

giving off one hydrogen ion as a monobasic acid or one hydroxyl ion as a monoacid base. The solubility product constants (p. 34) would be

$$[Al(OH)_2O^-] \times [H^+] = K_{solA} \quad (1)$$

$$[Al(OH)_2^+] \times [OH^-] = K_{solB} \quad (2)$$

A second and third hydrogen ion are also given off to a slight extent and likewise a second and third hydroxyl ion.

Applying the law of mass action it appears that an increase in the hydrogen-ion concentration would increase the basic ionization **(B)** in two ways, first by tending to reverse the ionization **(A)** (equation 1), and second, some of the hydrogen ions would combine with some of the hydroxyl ions removing them from the reaction as H_2O and allowing ionization **(B)** to proceed to the right (equation 2). If enough hydrogen ions are added, the second and third hydroxyl ions will be removed from the aluminum hydroxide and all the aluminum will be dissolved in the form of aluminum ions (Al^{+++}).

If the hydroxyl-ion concentration is increased, ionization **(B)** will be reversed and **(A)** will be increased as follows: First, the ionization **(B)** will be reversed by the increase in $[OH^-]$ (equation 2) and second, hydroxyl ions will combine with hydrogen ions to form water, thus decreasing the value of $[H^+]$ (equation 1) and allowing ionization **(A)** to proceed to the right. If the hydroxyl-ion concentration is made large enough all of the aluminum will go into solution as aluminate ion ($Al(OH)_2O^-$). In other words, aluminum will dissolve as aluminum ion in solutions with a low pH (p. 33) and as aluminate in solutions

of high pH. But somewhere in between it will be precipitated more or less completely. If aluminum hydroxide ionized only as indicated in the above equations (A) and (B) without the complication of secondary ionization the hydrogen-ion concentration at which it would be most completely precipitated—its isoelectric point—could be calculated (p. 37). Too little is known concerning the details of the reactions and the numerical values of the constants involved to warrant a mathematical treatment of this problem. An interesting attempt at such a calculation was made by Theriault and Clark.[1]

The Isoelectric Point.

These authors also determined experimentally a point which they defined as the isoelectric point. This was done by comparing the time required for the first appearance of a precipitate, with the pH of the solution in which the precipitate was formed. If the amount of "alum" added to a given volume was uniform throughout a given series of experiments and all other conditions such as temperature, etc., were controlled, only the pH being varied, then it was found that the time from the addition of the alum to the first appearance of the floc was always shortest in the test in which the pH had been adjusted to 5.5 or near that figure. Their experiments included solutions buffered with phosphates and solutions in which only the alum and lime were present. In different series the amount of alum was varied from 6 to 24 grains per gallon (100 to 400 ppm.).

They verified the experience of filter plant operators and predictions of Von Weimarn's theory (p. 48) to the effect that the greater the concentration of the precipitating substance (the potential supersaturation (x)) the more rapid will be the process of floc formation. For example, using 24 grains per gallon of alum the floc appeared in about one-half minute, while with 6 grains per gallon and at the same pH the floc appeared only after 10 minutes.

Previously[2] attention had been called to the importance of the hydrogen-ion concentration as a factor effecting the precipitation of alum floc and it had been pointed out that the control of coagulation by means of titrated alkalinity was insufficient.

Buswell, Edwards, Gallaher and McRoberts[3] attacked the problem

[1] *U. S. Pub. Health Rept.* **38,** 181.
[2] Wolman and Hannan, *Chem. & Met. Eng.* **24,** 728; **25,** 501; and Buswell and Edwards, *ibid,* **26,** 826.
[3] *Loc. cit.,* also *Ill. State Water Survey Bull.* 22.

of the determination of the "isoelectric point" of alum floc from a different angle. Their method was to determine the amount of aluminum remaining in solution after precipitation had taken place in solutions having different pH values. Their work covers three sets of conditions: (*a*) the precipitation of alum floc from buffered solutions with the determination of the amount of aluminum remaining unprecipitated in the decanted supernatant liquor; (*b*) the determination of the aluminum in the effluent from different filter plants which were known to be operating at different pH; and (*c*) the determination of the amount of aluminum in the effluent from a small experimental rapid sand filter which could be operated at any desired pH.

The results of these investigations indicated that there was no definite pH at which alum floc could be said to have a minimum solubility, but that less than 0.5 ppm. of aluminum oxide is retained in solutions having readings from pH 5.3 to pH 8.0. In the effluent from various filter plants the same broad zone of insolubility was observed but because of less ideal conditions the amount of alumina remaining unprecipitated was greater than in the laboratory experiments. In well operated plants the aluminum figured as Al_2O_3 is less than 2 parts per million between pH 6 and pH 8.

From these data it appears that alum floc has no isoelectric point but that it is very insoluble over a rather wide range and that therefore there is no reason for objectionable amounts of "residual alum" to pass through a filter except under very abnormal conditions.

From an operating standpoint other factors than insolubility must be considered. As stated above Theriault and Clark found that floc formation is most rapid at pH 5.5. Baylis [4] favored a zone between pH 5.7-6.6 for best operating results for a soft colored water and Hatfield [5] found a pH of 7.2-7.4 best for general operation of an uncolored, moderately hard, moderately turbid water.

The variation in the optima reported by different experimenters is further evidence that alum floc can hardly be said to have an "isoelectric point," at least not as gelatin and casein have. Rather there is a broad transition zone between the pH where its acid ionization predominates and the pH where its basic ionization predominates. In this zone a variety of properties are exhibited and one general property, very low solubility, is observed. Some chemical characteristics of the alum floc explain this zone to a degree at least.

[4] *J. Am. Water Works Assoc.*, **10**, 365.
[5] *J. Ind. Eng. Chem.* **14**, 1038.

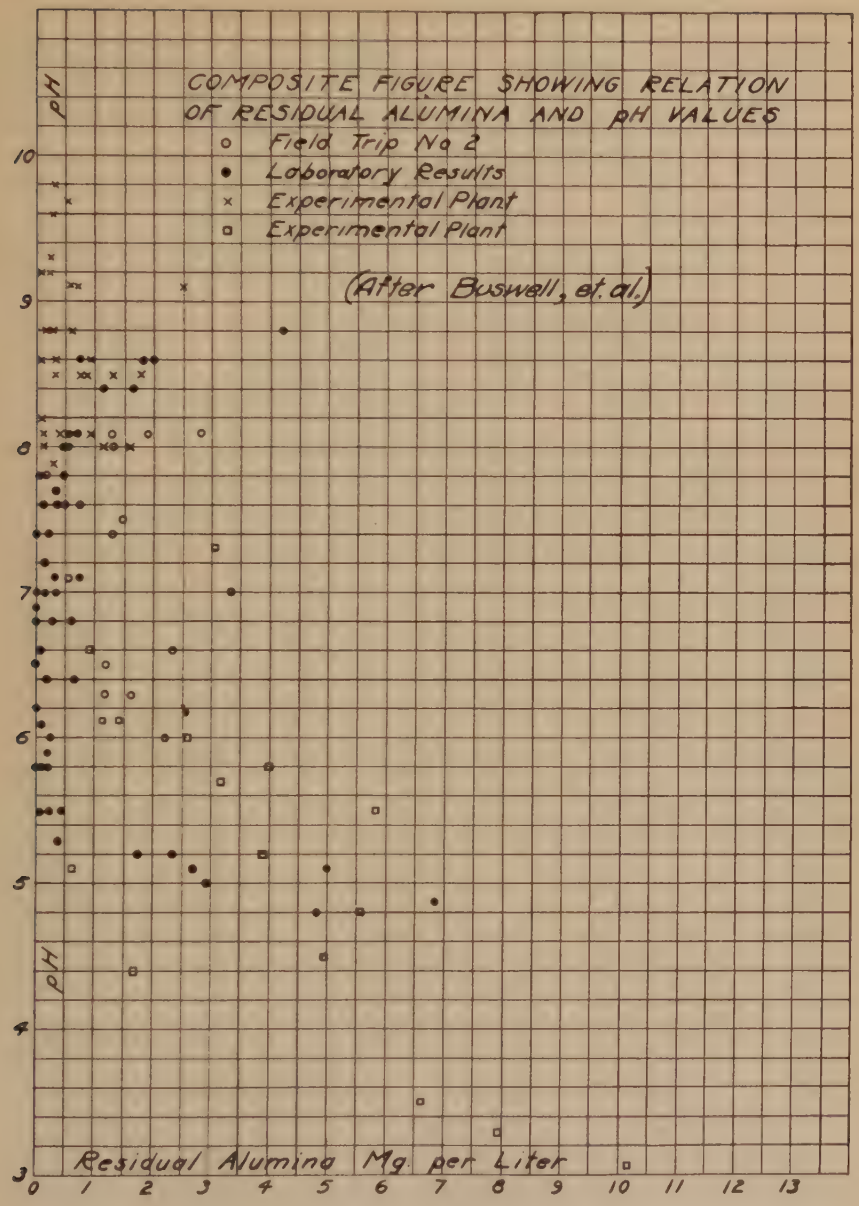


FIG. 22.—Composite Figure Showing Relation of Alumina and pH Values (after Buswell, *et al.*).

Composition of "Alum Floc."

It has been customary to refer to the precipitate which is formed when aluminum sulfate is added to natural water as aluminum hydroxide. Yet early investigators [6] realized that under certain conditions the reaction of the aluminum sulfate with the alkalinity was not always complete and that the precipitate sometimes contained sulfate. This was at first attributed to adsorption of aluminum sulfate by suspended particles since it appeared to vary directly with the turbidity of the water. A more plausible explanation is the formation of one or more of the possible basic sulfates, ($Al(SO_4)OH$; $Al_2(SO_4)_2(OH)_2$; $Al_2SO_4(OH)_4$, etc.). A number of chemists have reported on the composition of this precipitate as obtained under various conditions and all report basic salts. Of these Williamson [7] found that when one-third to two-thirds the calculated amount of alkali was added to a solution of potassium alum, a precipitate of the formula $5(Al_2O_3)\ 3(SO_3).15H_2O$ or $Al_2(SO_4)_3.8Al(OH)_3.3H_2O$ was formed. Miller [8] found the same sort of a precipitate under similar conditions but observed further that when five-sixths or more of the calculated amount of alkali was added the amount of sulfate in the precipitate decreased rapidly. When the amount of alkali was just over the theoretical quantity for the equation

$$Al_2(SO_4)_3 + 6NaOH \rightleftarrows 2Al(OH)_3 + 3Na_2SO_4,$$

the amount of sulfate in the precipitate became zero and the formula was apparently $Al(OH)_3$. All of these workers used potassium alum ($K_2Al_2(SO_4)_4.24H_2O$) instead of "filter alum" ($Al_2(SO_4)_3.18H_2O$) because the former could be more easily prepared in a high state of purity. But "alum" may not behave exactly like "filter alum" principally because of the extra sulfate radical. Furthermore, the concentration of the alum used experimentally was very much higher than is used in actual practice, being equivalent to 100 grains per gallon in the most dilute solutions.

Buswell and Gallaher [9] were unable to detect any appreciable amounts of sulfate in the sludge from several coagulating basins and Hopkins [10] found that above pH 6 a floc formed by a treatment of 1 grain per gallon contained no sulfate. It therefore appears that the precipitate actually formed in the average coagulating basin may still be considered as aluminum hydroxide. When heavy doses of alum are

[6] Fuller, G. W., *Water Purification at Louisville,* Van Nostrand, 1898.
[7] Basic Aluminum Sulfate, *J. Phys. Chem.* **27,** 284.
[8] *U. S. Pub. Health Rept.* **38,** 1895.
[9] *Loc. cit.*
[10] *J. Am. Water Works Assoc.* **12,** 405.

used or when precipitation is brought about in the acid range the floc undoubtedly contains a basic sulfate. There is also evidence that the phosphate, carbonate and silicate ions may be present in the floc in cases where they occur in the water before coagulation.

Colloidal Character of Alum Floc.

From Von Weimarn's theory of precipitation (p. 48) it follows that aluminum hydroxide will have a considerable tendency to form in a colloidal condition. Its solubility S is so slight that even in low concentrations the supersaturation X is considerable and therefore Rf will be large. But since S is so small Rg will be small and unless there is some substance present to increase the rate of clumping Ra, the tendency will be to form a sol instead of a floc.

Stable so-called "aluminum oxide" sols have been prepared by a number of workers and the effect of certain coagulating agents determined. These sols apparently have the composition $X\,Al_2O_3 . W\,H_2O . Y\,AlCl_3 . Z\,AlCl_2^+ + Z\,Cl^-$, since a similar formula has been assigned to the so-called ferric oxide sol by Thomas and Frieden.[11] In words instead of symbols we would say—the colloidal particles are composed largely of aluminum hydroxide with a small amount of aluminum chloride, a minute portion of which is ionized to form $AlCl_2^+$ ions which are held to the particle and give it a positive charge, and Cl^- ions which diffuse a short distance into the solution. The aluminum chloride and more particularly the $AlCl_2^+$ is the "solution link" and is apparently essential to the stability of the sol since if it is removed (by dialysis) the sol will coagulate. On the other hand an excess of electrolytes will cause the sol to coagulate.

Effect of Anions on Alum Floc.

The effect of electrolytes on colloids has been discussed on page 49, where it was pointed out that positive sols are coagulated by negatively charged ions and vice versa. It was also noted that monovalent ions were much less effective coagulants than divalent ions and that divalent ions were less effective than trivalent ones, etc.

Table 17 gives some data developed by Freundlich on the effect of certain ions on "aluminum oxide" sol.

A study of the effect of anions on the coagulation of alum floc has been made by Miller,[12] which contains data of more immediate interest.

[11] *J. Am. Chem. Soc.* **45**, 2522 (1923).
[12] *U. S. Pub. Health Rept.* **40**, 351.

This investigation showed that the pH zone in which aluminum is most completely precipitated is dependent upon the acid ions present. Table 18 was compiled from Miller's data.

TABLE 17.—*Amounts of Anions Adsorbed in the Coagulation of Aluminum Oxide Sols.**

	Threshold value, millimol per liter	Millimol adsorbed per gm. Al_2O_3	Milliequivalent per gm. Al_2O_3
Salicylate	8	0.46	0.46
Picrate	4	.275	.275
Oxalate	.36	.275	.55
Ferricyanide	.10	.14	.42
Ferrocyanide	.08	.11	.44

* Patrick, in Taylor's *Treatise on Physical Chemistry*, p. 1310.

The shift of the zone of complete coagulation with the change in acid ion explains the variation in "isoelectric" points reported by various investigators who worked with natural waters. The narrowing of the zone when the alum dose in the above-mentioned experiment was de-

TABLE 18.—*Effect of Anions on the Coagulation of Alum Floc.*

Anion		pH at which coagulation is complete		
		Treatment 100 gr. per gal.	Treatment 10 gr. per gal.	Treatment 5 gr. per gal.
Sulfate	SO_4^{--}	5.2-7.6		5.8-7.2
Phthalate	$C_8H_4O_4^{--}$	5.8-8.8		
Chromate	CrO_4^{--}	5.9-8.8		
Chloride and Ammonium Chloride	$Cl^- + NH_4Cl$	6.2-9.4		
Carbonate	CO_3^{--}	6.4-8.7		
Chloride	Cl^-	7.8-8.5	8.1-8.2	
Oxalate	$C_2O_4^{--}$	8.8-9.0		
Phosphate	PO_4^{---}	*4.8-8.1		

* Filtrate milky.

creased from 100 grains per gallon to 5 or 10 grains per gallon is worthy of note. Since even 5 grains per gallon is a rather high dose it is obvious that the actual zone limits given in Table XII cannot be used in practice. The data indicate more clearly than has been done heretofore what factors affect the position of the precipitation zone so that it may now be determined for individual cases with some certainty. The data on the chloride ion agree with the general knowledge of the

FIG. 23.—Rock Island, Illinois, Water Works.

fact that when aluminum chloride is used a sol is very likely to result instead of a precipitate.

Miller also showed that while the point of most rapid floc formation in the presence of sulfate ion was pH 5.5, it shifted to pH 8 when chloride ion was the only acid ion present.

He found that there was a definite relation between the amount of anion per gram of floc and the concentration of that anion in the solution from which the floc was precipitated and that when more than one anion was present there was a constant relation between their relative concentrations in the solution and in the floc. The exact mechanism of the reactions of anions with alum floc is open to question. Miller [13] considers that the aluminum salts of the anions are dissolved in the aluminum hydroxide of the floc forming solid solutions. His data, however, fail to give the proper constants for this condition (the variations were as much as a thousand-fold). The author has recalculated Miller's data using the adsorption isotherm formula and obtained much more uniform constants. Since there is an objection to the assumption of the existence of a solid solution unless mixed crystals of the constituents can be obtained for observation, it seems advisable to consider these reactions as adsorptions.

Further, it has been shown [14] that the minimum effective concentration of a precipitating ion depends upon the degree to which it is adsorbed, which suggests that the varying effects of the different anions on the coagulation of the floc is related to their adsorption by the floc.

Factors Affecting Rate of Floc Formation.

Since according to Von Weimarn's theory (p. 48) a very insoluble substance like aluminum hydroxide tends to form sols instead of precipitates, it is not surprising that in filter plant operation difficulty is occasionally encountered in producing a floc.

Referring to the discussion of colloid formation (p. 48) we recall that minute crystals of the insoluble substance are formed very rapidly. From this point they may increase in size either by recrystallization—growth of large crystals at the expense of smaller ones (Rg)—or by the clumping together of the smaller crystals (Ra). In the case of aluminum hydroxide as formed under practical conditions the concentrations of the ions of which the precipitate is composed are so low that the rate of growth by recrystallization is practically zero. These micro-crystals do not possess kinetic motion as molecules do, so that growth by the second process, namely, aggregation, depends upon some

[13] *Loc. cit.* [14] Patrick, *loc. cit.*

force like stirring, convection currents or sedimentation to bring the particles into contact with each other. Sedimentation or settling of the particles does bring them into contact with other particles and flocs are thus formed, but a much more effective means of bringing these micro-crystals together so that they will form flocs is to stir the liquid mechanically. The advantage of stirring is pretty generally recognized by engineers and it is not the purpose of this discussion to consider the various methods of producing agitation. A relatively slow wide-sweeping motion has been found most effective. As soon as the velocity becomes great enough to cause turbulence the efficiency drops off.[15]

Temperature differences will set up convection currents which on account of their stirring effect aid floc formation. An increase in temperature will also increase the kinetic motion of molecules and decrease the viscosity of the water. Both of these effects tend to increase the rate of growth of the floc by recrystallization. The decrease in the viscosity also lessens the resistance to stirring so that growth of floc by aggregation is facilitated.

The greater the number of micro-crystals of aluminum hydroxide in a given volume the greater will be the probability that two or more will come together during stirring or sedimentation and thus form flocs. Now the number of micro-crystals is dependent upon the concentration of "alum," that is, the dosage, and it is well known that an increased dosage results in quicker floc formation.

Changes in Alkalinity and pH.

The chemical reactions taking place during coagulation have from time to time been represented in textbooks and technical articles by various styles of chemical equations. All of these show in the main that 8 mg. per liter of alkalinity will react with 1 grain per gallon of filter alum, forming aluminum hydroxide. As is very well known, none of these reactions go to completion, but we have instead a number of reversible reactions, each of which depends for its final equilibrium upon all of the others. Such complex systems seem to be best represented graphically by the method used by Smith[16] as shown in Figure 24.

The heavy arrows indicate the direction of the predominating reaction. The substances toward which the light arrows point will be present in relatively small amounts. It should be recalled in this connection that any secondary reaction which tends to remove a product

[15] *Chem. & Met. Eng.* **27**, 1176 (1922).
[16] *Introduction to General Inorganic Chemistry*, 3rd Ed. Chap. XIX.

of a primary reaction will increase the amount of the primary reaction in the direction of the formation of the removed product. Numerical coefficients such as are used in "balancing" ordinary chemical equations have been omitted to avoid complicating the diagram. This formulation shows the interdependence of these reactions. It also emphasizes that in each of these equilibria the hydrogen ion plays a part either directly or through its reciprocal relation to the hydroxyl ion. The

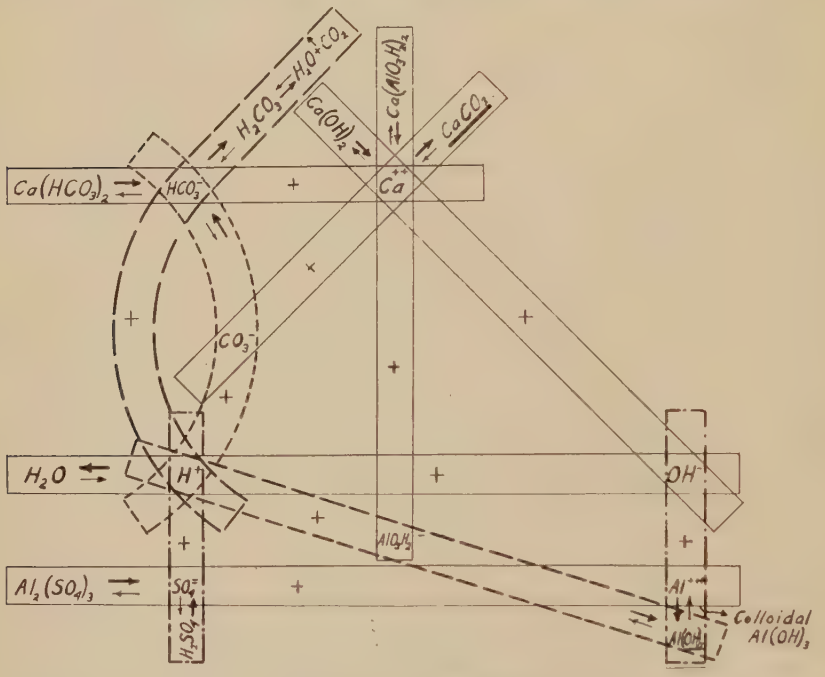


FIG. 24.—Reactions in Coagulation Basin.

relation between alum and alkalinity is shown here as in other representations, but it also appears that the loss of carbon dioxide with the precipitation of calcium carbonate may cause a decrease in the alkalinity, and that the addition of lime may cause a net decrease in the alkalinity due to this same precipitation of calcium carbonate. On the other hand, the formation of colloidal alumina instead of the precipitate would tend to offset the decrease in alkalinity.

An inspection of Table 19, which has been compiled from data from 20 filter plants, shows examples of all three of the above-mentioned cases. At four out of nineteen of the plants studied (2, 10, 13, 14) the decrease in alkalinity corresponded to 8 mg. per liter per grain

per gallon of alum used. At nine plants (1, 7, 9, 12, 15, 17, 18, 19, 20) the decrease in alkalinity was greater than the calculated. This group includes, as would be expected, the three plants at which lime as well as alum was added. At six plants the decrease was less than the calculated.

TABLE 19.—*Alkalinity and* pH *Changes in Filtration.*

Town	Alkalinity		Decrease		pH	
	Raw Water	Filtered Water	Found	Calculated	Raw Water	Filtered Water
1	56	62	—6	—12	7.8	8.1
2	116	110	6	5.6	8.3	7.7
3	178	170	8	11.2	8.3	7.5
4	192	186	6	8.0	8.0	7.5
5	180	176	4	8.8	7.6	7.5
6	79	84	—5	2.96	7.5	7.5
7	134	116	18	14.80	8.0	7.4
8	...	124	..	....	..	..
9	126	112	14	—1.4	7.9	7.3
10	130	108	22	22.4	7.9	7.3
11	160	154	6	21.6	7.3	7.2
12	68	58	10	7.2	7.5	7.1
13	82	71	11	12.0	8.1	7.0
14	58	54	4	3.68	7.5	6.9
15	132	94	38	24.0	7.9	6.8
16	48	42	6	16.0	7.2	6.8
17	54	24	30	16.0	8.4	6.2
18	46	24	22	12.0	8.5	6.2
19	60	16	44	0.8	7.2	6.1
20	24	2	22	16.8	6.8	6.0

In addition to those already mentioned we submit the following list of factors which would tend in a measure at least to produce the deviations cited above. Decrease in alkalinity would be caused by: Removal of colloidal iron and aluminum hydroxide and carbonates; removal of alkaline turbidity; titration error caused by adsorption of acid on colloids during titration;[17] excessively acid alum. Factors tending to offset the decrease in alkalinity are: Use of basic alum; precipitation of basic aluminum sulfate instead of aluminum hydroxide; resolution of calcium carbonate previously deposited on the sand.

To follow the change in calcium and magnesium content during treatment with alum and lime, a few determinations were made[18] of these substances, with results as shown in Table 20.

In calculating the decrease of alkalinity due to reaction with alum when lime is used, the practice has been to consider that lime tends to

[17] Pirnie, Malcolm, *Can. Eng.* 41, No. 19 (1921).
[18] Buswell and Gailaher, *Ill. State Water Survey Bull. 22.*

TABLE 20.—*Theoretical and Actual Reduction in Alkalinity on Treatment with Alum and Lime.**

Sample	1		2		3		4		5	
	Raw	Effluent	Raw	Effluent	Raw	Effluent	Raw	Effluent	Raw	Effluent
pH value	7.6	8.0	7.7	8.0	7.7	8.5	7.7	8.6	7.7	8.8
Alkalinity:	*parts per million*									
methyl orange	238	236	242	246	246	220	250	270	250	240
phenolphthalein	0	0	0	0	0	10	0	10	0	10
Free CO_2	8	5	5	3	5	0	8	0	4	0
Ca, as $CaCO_3$	267.1	279.6	272.4	231.3	262.5	234.9	267.1	285.0	271.5	250.0
Mg, as $CaCO_3$	184.5	181.8	187.6	184.5	190.6	185.4	180.4	186.3	186.3	182.7
Lime added, as $CaCO_3$	23.9		32.8		75.1		40.7		63.9	
Alum added (in grains per gallon)	1.0		1.0		1.0		1.0		1.0	
Actual decrease in alkalinity		2		−4		26		−20		10
Calculated decrease if Ca and Mg were not precipitated		−15.9		−24.8		−67.1		−32.7		−55.9
Calculated decrease correcting for amount of lime actually used to precipitating Ca and Mg		−1.8		2.2		41.0		−16.6		33.0

* Bushwell and Gallaher, *Ill. State Water Survey Bull. 22*, p. 100.

offset decrease in alkalinity. The contrary, however, may be true, since lime will precipitate calcium and magnesium from the bicarbonates of these metals and also react with carbon dioxide in the following manner:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$
$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O$$
$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$$

Twice as much lime is required to remove the same amount of $Mg(HCO_3)_2$ alkalinity as is required for $Ca(HCO_3)_2$ alkalinity. The following method of calculation takes this point into account:

Let $Ca\overline{CO_2}$ = lime required for CO_2 (This will not be included if there is free CO_2 in the effluent.)
Ca_1 = calcium in the raw water.
Ca_2 = calcium in the effluent.
Ca_L = calcium added as lime.
Mg_1 = magnesium in the raw water.
Mg_2 = magnesium in the effluent.

$\underline{Ca}\lceil CO_2 + 2(Mg_1 - Mg_2)$ = calcium of the lime used up in ways not affecting the calcium of the water.

$Ca_1 + Ca_L - \underline{Ca}\lceil CO_2 + 2(Mg_1 - Mg_2) - Ca_2$ = amount of calcium precipitated.

Decrease in alkalinity would be

$$A_3 = (Ca_1 - Ca_2) + (Mg_1 - Mg_2) + (\text{alum})$$

assuming 8 ppm. is the alkalinity reduction due to one grain per gallon of alum. This will not affect the total calcium content of the water.

It will be seen from Table 20 that, if the precipitation of calcium and magnesium is taken into account, the actual reduction in alkalinity approximates the theoretical more closely. Discrepancies that still exist may be due to a certain amount of adsorption of the different ions.

Mechanism of Purification Reactions.

From the foregoing discussion of the chemical and colloidal characteristics of aluminum sulfate it appears that it has the following properties which may be useful in water purification. (1) It reacts with the alkaline substances found in most natural waters to form a flocculent precipitate which may in a mechanical way sweep impurities out of the water. (2) This floc, because of its large surface, may adsorb large amounts of dissolved or colloidal matter from the water or it may coat the sand grains of the filter and thus act as an adsorbent. (3) Aluminum sulfate hydrolyzes when dissolved in water yielding hydrogen ions, i.e., it is in effect a weak acid. Hence it may be used, though not necessarily economically, where acidity is desired. (4) It yields the trivalent positive aluminum ion (Al^{+++}) which has been shown to be very effective in precipitating negative colloids. (5) It yields the divalent negative sulfate ion which has a precipitating effect on positive colloids, such as "colloidal iron" or "colloidal alumina."

When the manifold characteristics of "alum" are considered it is not surprising that there is some confusion as to what its action is in any given case. When turbidity is removed it is probable that reactions (1), (2), and (4) all play a part. The turbidity is composed of negative colloidal particles in most cases. The positive aluminum ion will react with these, breaking their solution link and causing precipitation. But this reaction would appear to be of secondary importance since present data indicate that a pH of about 7 is the best for turbidity removal and at that pH the number of aluminum ions has practically reached a minimum. Reactions (1) and (2), the mechanical and adsorptive actions of the floc, are apparently the important ones. A

further careful investigation of the mechanism of turbidity removal is needed.

Since color is more effectively removed in the lower pH ranges [19] where there is a larger amount of aluminum ion present and where floc formation is not so complete the assumption would be that aluminum ion is the effective agent. This assumption has been confirmed by Miller,[20] who showed that the color produced either by artificial humus, soil extract or tea is a negative colloid and that it is precipitated by positive ions. These precipitation reactions follow the valency rule hence the trivalent aluminum ion is very effective. Since it is present in appreciable concentrations only in the acid range it is advisable to add the alum, with acid if necessary, to precipitate the color and later add alkali to prevent corrosion and remove any excess alum.[21] A high pH may actually result in a redispersion of the color, probably by breaking the aluminum color complex.

Various Modifications of Alum Treatment.

The chemical reasons for the adjustment of the pH have already been discussed. Langelier has taken out a patent on this mode of treatment [22] although he does not appear to have been the first to have used it. The savings resulting from this control have been given by Baylis [23] as $125,000 per year at Baltimore. The more effective coagulation has relieved the load on the filters at Waterford [24] to such an extent that there has been a saving of 17 percent in wash water.

Aëration of the water immediately after treatment with alum has been found advantageous by Bunker [25] and by Pirnie [26] resulting in more efficient coagulation. The aëration produces very effective mixing at a stage in the process when it is most needed and also results in liberation of excess carbon dioxide formed by the reaction of aluminum sulfate with carbonates.

The addition of 0.6 to 1 part per million of chlorine [27] before filtration increases the efficiency of the alum when soft colored waters are treated. The chlorine lowers the pH and as was shown by Miller [28]

[19] Norcom, *J. Am. Water Works Assoc.*, **11**, 97; Baylis, *ibid.* **10**, 365.
[20] *U. S. Pub. Health Rept.* **40**, 1472.
[21] See Norcom, *loc. cit.*
[22] U. S. Pat. No. 1,465,137.
[23] *Loc. cit.*
[24] Anon., *Publ. Works*, **55**, 145.
[25] *Eng. Rec.* **75**, 334 (1917).
[26] *Eng. News-Rec.* **90**, 883 (1923).
[27] Gammage, *Eng. News-Rec.* **88**, 391; Weston, *J. Am. Water Works Assoc.* **11**, 446.
[28] *Loc. cit.*

increases the aluminum-ion concentration both of which are desirable in color removal. The chlorine undoubtedly has a bleaching effect on the color but this phase of the reaction has not been investigated. Pre-chlorination to improve bacterial efficiency has been used at the slow sand filters at Poughkeepsie, N. Y., with the drifting sand filters at Toronto, and elsewhere.

The application of the alum in two successive doses as it enters a first and second coagulation basin respectively results in better efficiency of the filters with a smaller total amount of alum used. This process is referred to as "double coagulation" [29] and the amount of alum used in the first treatment is 60 to 75 percent of the total. A plant built for double coagulation requires less basin area than one built for plain sedimentation followed by single coagulation. Since the removal of impurities depends upon contact between the floc and the suspended particles or between the aluminum or sulfate ions and the particles of impurities the process is relatively slow and in heavily polluted waters may not be completed by the time the floc has settled. Producing the floc in two successive stages increases the chance for contact between the impurities and the floc and is equivalent in some respects to stirring, the advantages of which have already been discussed.

A number of liquid preparations have been placed on the market recently which on diluting produce a floc more quickly in general than alum does when added in the ordinary way. They are variously referred to as "aluminum hydroxide solution," "colloidal alumina," "sodium aluminate" and other trade names. Coxe [30] describes such a reagent which is made by adding a solution containing 1 part of soda ash (Na_2CO_3) to a solution of 4 parts of "alum" ($Al_2(SO_4)_3 \cdot 18H_2O$). "Coagol" described by M. N. Spenser [31] is apparently similar. This partial neutralization of the alum produces a sol which coagulates on dilution. These preparations would be more expensive to ship due to the amount of water they contain and the added soda would also increase the cost. Some of them will set to a gel in a few weeks. In small plants where convenience is more important than cost of chemicals and in places where the acid property of alum is of no advantage they will undoubtedly be found useful. Some experiences with these preparations are given in the Fourth Annual Report (Nov., 1924) of the Ohio Conference on Water Purification. They present more unfavorable than favorable data. Since all recent investigations have

[29] Sheehan, *J. Am. Water Works Assoc.*, **12**, 442.
[30] *Chem. & Met. Eng.* **29**, 279.
[31] *Chem. Age*, N. Y., **32**, 31.

pointed to acid conditions as the more favorable to coagulation it would be surprising if these alkalinized preparations should be found advantageous. Recently good results have been reported with waters of low turbidity which coagulate slowly with alum. Solid sodium aluminate is now on the market.

Coagulation with Iron Salts.

Although not so widely used, ferric hydroxide apparently has about the same properties as a purifying agent as does aluminum hydroxide. Chemically it differs from the latter in that it does not form a soluble ferrate analogous to the aluminate. It does not dissolve, therefore, at high pH values. Miller [32] has made a study of the effect of pH on the precipitation of both ferrous hydroxide from ferrous sulfate and of ferric hydroxide from potassium-ferric alum. When ferrous sulfate is treated with caustic soda solution free from oxygen the pH rises quickly to 7.5 and then more slowly to pH 8 which point it reaches when about three-fourths of an equivalent of caustic soda has been added. When one equivalent of NaOH (one half that required theoretically) has been added, the pH stands at 11. From this point it rises slowly to 11.8 with the addition of NaOH up to the amount required by the equation: $FeSO_4 + 2NaOH \rightleftarrows Fe(OH)_2 + Na_2SO_4$. These data indicate the formation of a basic sulfate which on further addition of alkali changes to the hydroxide. This assumption is confirmed by the fact that at pH 7.9 the sulfate-iron ratio is 0.1 and on complete neutralization this ratio is 0.

When ferric sulfate is treated with NaOH according to the equation $\frac{1}{2}Fe_2(SO_4)_3 + 3NaOH \rightleftarrows Fe(OH)_3 + 1\frac{1}{2}Na_2SO_4$ the pH rises from 3.0 to 3.5 on the addition of $2\frac{1}{2}$ equivalents of NaOH and then jumps to pH 7.7 when 3 equivalents are added. The sulfate-iron ratio is 0.2 in the precipitate formed when one equivalent has been added but drops to 0.0 when 3 equivalents of NaOH are used. The precipitates formed when less than the theoretical three equivalents are used are lighter brown and show a greater tendency to form sols. As in the case of aluminum the chloride forms a sol which is precipitated incompletely and with difficulty. The presence of the acid radicle in the basic salts acts as a solution link tending to prevent precipitation. It is therefore apparent that best coagulation would occur at pH 7.7 or higher.

In practice neither of the two cases just discussed is used. But ferrous sulfate (copperas) is used in the presence of oxygen which

[32] *U. S. Pub. Health Rept.* **40**, 208 (1925).

oxidizes it to the less soluble ferric hydroxide. A pH somewhat higher than 7.7 is required for the formation of the ferrous hydroxide and it is also known that a high pH favors the oxidation of this compound to the ferric state. The exact course of these reactions has not been worked out but experience has shown that a "pink to phenolphthalein" is favorable. The addition of lime is required to meet this condition. This is in the pH range where the precipitation of calcium carbonate (softening) occurs and since it precipitates rather slowly it frequently fails to settle out in the coagulation basin but passes over to the sand beds causing incrustation. If the lime treatment is carefully controlled this effect may be kept to a minimum. C. A. Brown [33] recommends a lime treatment which neutralizes the free carbon dioxide, the ferrous sulfate, and enough of the bicarbonate so that the treated water contains not over 6 ppm. of the normal carbonate ($CaCO_3$).

The formation of ferric hydroxide from ferrous sulfate is dependent upon the presence of oxygen as well as hydroxyl ion. The ferrous sulfate cannot be successfully used with septic sewage or high organic wastes devoid of oxygen on this account. The ferrous hydroxide is soluble to the extent of about seven parts per million and would be discharged in the effluent to be precipitated later when the liquor became aërated. Since the pH of the solution affects both the precipitation and the oxidation reactions and since a certain minimum content of oxygen is necessary, the determination of the optimum conditions for precipitation is complicated.

The commercial ferrous sulfate or sugar sulfate ($FeSO_4 . 7H_2O$) has usually lost some of its water of crystallization and its content of $FeSO_4$ averages 102 percent of the calculated. The large crystals formerly sold carried an excess of water, etc., and were 94 to 96 percent pure.

In some plants the incrustation of the sand is avoided by changing occasionally from sulfate of iron to sulfate of aluminum. The free carbon dioxide formed as a result of the acid character of the alum dissolves away the calcium carbonate from the sand grains.

[33] *Manual of the American Steel & Wire Co.*

Chapter XII.

Filtration and Disinfection.

Filtration.

The filtration of water is not a straining or sifting action but rather a surface adsorption. The particles removed are much smaller than the openings between the particles of the filter material but they stick to the surface or get caught in the angles and turns of the tortuous path through the filter.

Types of Filters.

Filters may be of the pressure type or the gravity type. Pressure filters are made up in steel shells and are attached directly to the pressure main. Alum is added by means of some sort of injector device without allowing any time for coagulation. They are usually built in relatively small units. In filtering material and operation they resemble the gravity filters.

The gravity or open type filters are so constructed that the water flows through them by gravity. There are three different designs (1) The "double" filter or as it is sometimes called the "pre-filter" or the Peuch-Chabal system;[1] (2) the "slow sand" filter, and (3) the "mechanical" or "rapid sand" filter. All three are alike in that the filtering medium is a submerged bed of sand or gravel through which the water passes.

In the first or "Peuch" design three of four filters are provided. The first is filled with rather coarse gravel, the second with finer, etc., and the last filter is of fine sand. The first filter is rather small and the rate of flow may be 100 million gallons per acre per day. As the filters become finer grained the rate decreases until the sand bed is reached, where the rate is about four million gallons per acre per day. In this type of filter the heaviest load is put upon the coarser-grained material and the water is partially purified before it reaches the fine sand, hence the filters do not clog so quickly and can be operated at

[1] Williamson, *Eng. News* 60, 236 and *Eng. News-Rec.* 92, 205 (1924).

(*Courtesy Alvord, Burdick & Howson*)

Fig. 25.—General View of a Water-Treatment Plant.

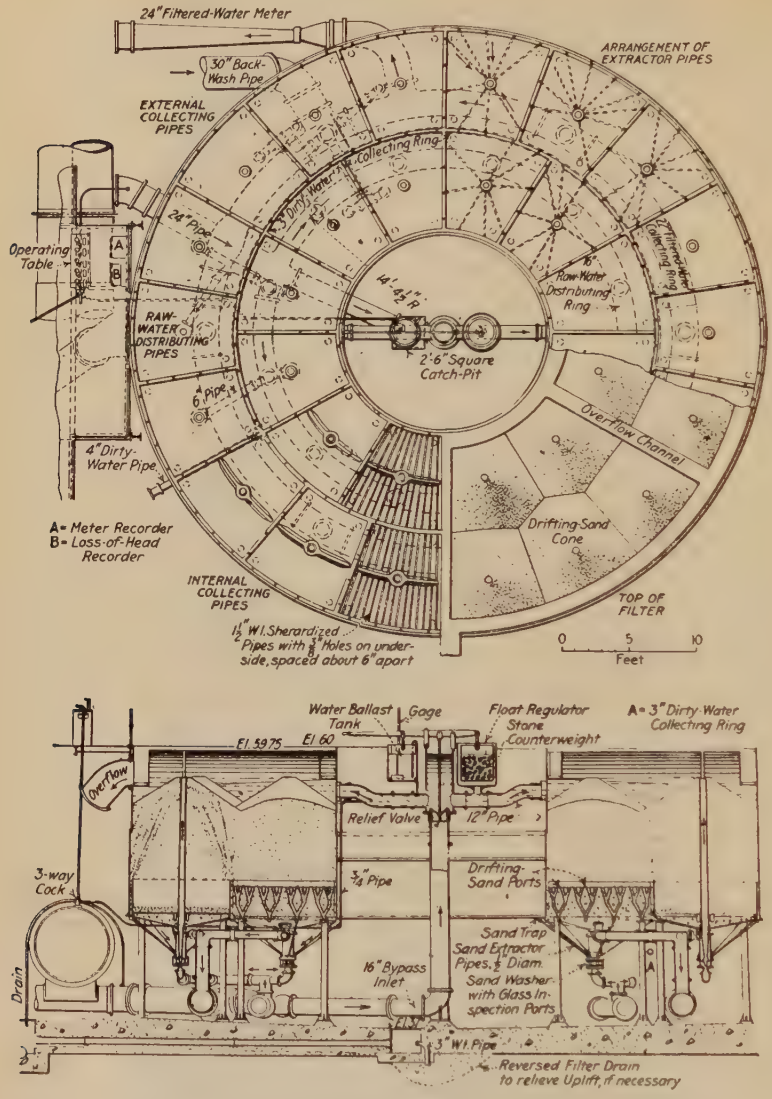


FIG. 26.—Details of Drifting-Sand Filter at Various Horizontal and Vertical Planes.

higher rates. From a theoretical point of view this would seem to be the correct procedure but so far these filters have not proven popular.

The slow sand filter was developed before the use of coagulants and was operated at a slow rate (2-3 million gallon/acre/day). It con-

sists of a bed 30 to 50 inches deep of fine sand (0.20 to 0.40 mm. effective size) supported on gravel. The accumulation of impurities on the surface forms a sort of film which increases the efficiency of the filter. In time these filters become so clogged that they have to be shut down and the upper layer of sand washed. Where this type of filter is still in use alum is now generally employed instead of depending on the naturally formed film.

The mechanical or rapid type of filter has been used in practically all of the filter plants which have been built in recent years. These filters differ from the slow sand filters in two important respects. They are provided with a system of pipes at the bottom of the bed through which water can be forced upward through the filter thus "back washing" it in a few minutes instead of shutting down the filter and taking the sand out to wash it. And a greater rate of filtration, 150 million gallons/acre/day, is employed. This is made possible by the use of a slightly coarser sand (0.30-0.40 mm. effective size), a pretreatment with alum, a shallower bed of sand (30-36 inches) and a greater depth of water over the sand. The "back washing" is sometimes preceded by agitating the bed mechanically or with compressed air to increase its effectiveness.

Both the slow sand and mechanical filters are "upside down" from a theoretical standpoint in that the heaviest load is thrown on the finest material while the coarser material, the gravel at the bottom, has little or no purifying action. In fact most of the purification is accomplished in the first inch or two of the sand. An investigation of depth of sand at St. Louis [2] showed that a 12-inch bed could be used and that there was no advantage in having more than 24 inches of sand. Sand finer than 0.38 mm. was not found desirable.

Character of Purifying Action of Filters.

The purifying action of a filter is apparently of both a physical and a colloidal character. Particles which are much smaller than the size of the openings between the sand grains may be held back as logs are often caught in a jam in a stream. The size of a single log is only a small fraction of the width of the stream, yet if a large number of logs were left to float unattended it is doubtful whether more than one or two would reach the mill, certainly not if the distance to be travelled were twenty-five to fifty miles of the average northern stream. Similarly, particles of turbidity and even bacteria are caught in the twisted path through the filter.

[2] Report of Water Commissioner E. E. Wall, 1924.

This passage through the sand causes a mixing which helps to complete the final stages of coagulation. Coagulation is further aided by the fact that the sand presents a very large surface to the liquid thus affording opportunity for a considerable amount of adsorption of both dissolved and colloidal material. The sand grains in contact with the average natural water which is slightly alkaline acquire negative charges due probably to the adsorption of hydroxyl ions. The alum floc is positively charged due to the positive ion which is the solution link

(*Courtesy International Filter Co.*)

FIG. 27.—International Sampler Table and Depth Gauge.

so that there is a tendency for it to combine with or adsorb on the sand grains. It was pointed out in the discussion of coagulation that aluminum hydroxide has certain properties which tend toward sol formation. The filter therefore is essential to the completion of the coagulation process as well as for the purpose of arresting larger particles which do not settle in the coagulation basin.

Due to the friction in passing through the filter there is a loss of head which increases as the filter becomes clogged. When this loss of head becomes too great the filters are back-washed with filtered water. The length of runs between washings is dependent upon the success of the preliminary treatment which the water has received. With proper adjustment of the coagulant and a well designed basin a twelve to twenty-four hour run may be made and the amount of wash water kept down to 5 percent or less of the total filtered. Longer runs

are recorded in cases where the pre-treatment is exceptionally good. Since the effectiveness of a filter increases with use the loss of head is the factor which decides the time for washing.

Clark's Impregnated Filters.

Although the evidence already cited indicates that color removal is due to aluminum ion, Clark [3] has reported good results when clear, soft, colored water is filtered through a slow sand filter whose grains have been coated with aluminum or ferric hydroxide. Since the color removal is accomplished at a pH of 6+ there cannot be a very large amount of aluminum ion present. The color removal here appears to be due to the formation of a chemical combination or an adsorption compound between the color and the iron or aluminum hydroxide. This combination is readily broken up by dilute solutions of alkalis so that the color can be removed and the bed regenerated. Apparently there is no solution of alumina during this regeneration unless too strong an alkali is used.

Drifting Sand Filter.

An unusual type of filter is described by Nasmith & Adams [4] in which the dirty sand is removed continuously and is returned, clean, with the raw water. This filter has given good results for over ten years in the one installation but the type has not come into general use. Because the sand "drifts" from the point where it enters to the point where it is drawn off to be washed, this filter has been called the "drifting sand filter." Its advantages are mechanical rather than chemical and a detailed discussion of them will not be given here.

Difficulties in Filter Operation.

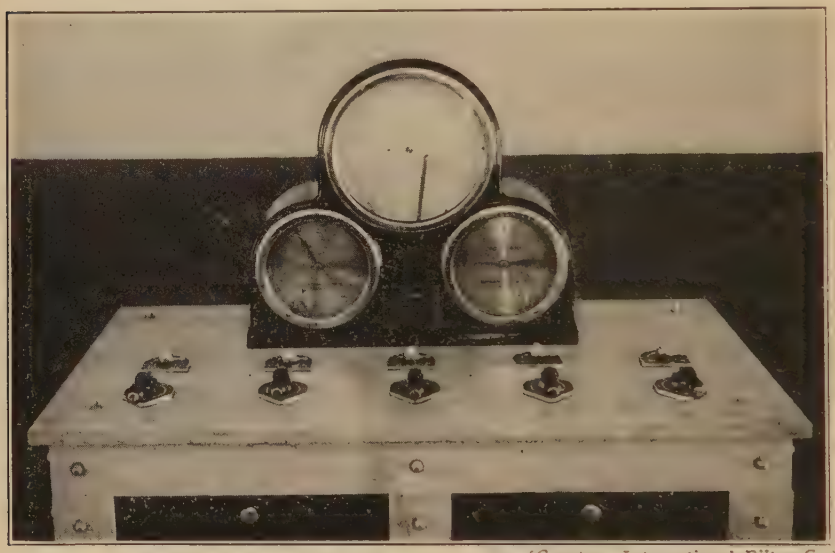
Among the various problems in the operation of filter plants some which have a chemical explanation may be mentioned.

Deposit of Impurities. In ordinary operation sand beds tend to become impregnated with alumina and impurities present in the water. This has been considered a disadvantage with rapid filters because of the loss of head. Green [5] has suggested the use of strong caustic with steam to remove this coating. For a filter containing 40 tons of sand and 12 tons of gravel he used 350 pounds of caustic soda

[3] *J. New Eng. Water Works Assoc.*, **36**, 385; **38**, 84.
[4] *Eng. Rec.* **71**, 464 (1915).
[5] *Eng. Contr.* **62**, 1270 (1924).

and 1000 pounds of soda ash and enough water to cover the sand an inch. The filter was steamed out with live steam for two days after which the sand was found "as clean as new." Although no data are given we may assume that this treatment would give a pH in the bed high enough to dissolve alumina as the aluminate.

Air binding. "Air binding" occurs when gas (usually air) collects in bubbles in the filter bed. These bubbles cut off the portion of the bed in which they form and reduce proportionately the efficiency of the filters. The water as it comes to the filter is presumably saturated with air at atmospheric pressure. Within the filter it is subjected to a

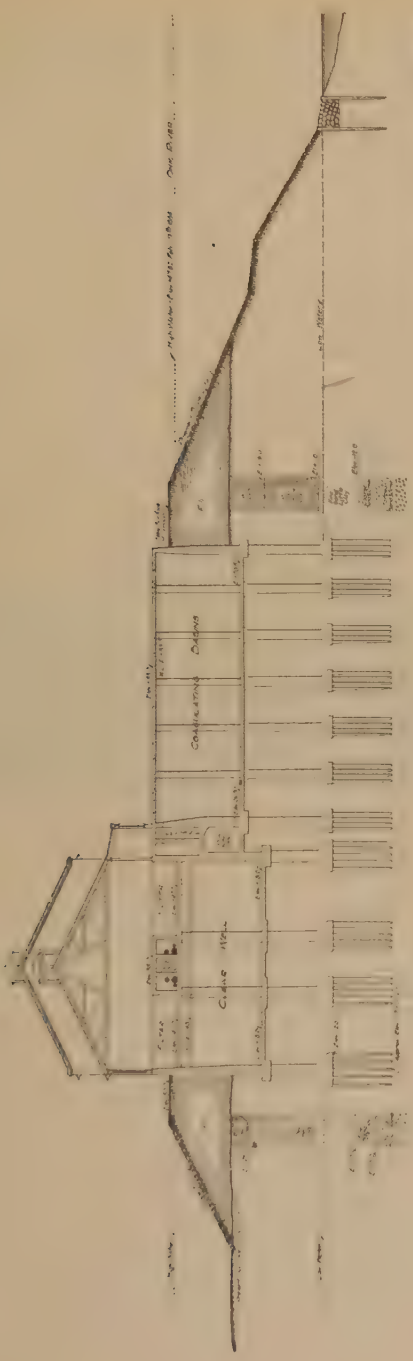


(*Courtesy International Filter Co.*)

FIG. 28.—Tuscaloosa, Ala., Plant. Top View of Operating Tables.

partial vacuum which lowers the solubility of the air so that it collects in bubbles.. This "negative head" within the filter is similar to the suction produced by the column of water in the stem of a filter funnel. If the water is cold and saturated and the filter house warm the solubility of the air is decreased still further and conditions will be worse.

It is well known that a liquid will frequently remain supersaturated for some time and occasionally indefinitely unless it is "seeded" or the precipitation started in some way. The presence of the sand grains with their edges and corners furnishes starting points for the formation of bubbles just as they would for the formation of crystals if the solution were supersaturated with respect to a solid.



(Courtesy Alvord, Burdick & Howson)

FIG. 29.—Cross-section of a Water-treatment Plant.

Surface Shrinkage. In some filters difficulty is encountered due to a cementing or compacting of the sand especially near the surface. This may be observed when the bed is washed and is usually accompanied by a surface shrinkage causing cracks in the top of the filter and a drawing away from the side walls. This condition of course results in a decrease in the efficiency of the filter. The problem has been investigated by Wolman and Powell;[6] Gavett[7] and Bayliss.[8] These papers express varying opinions as to its cause. From all evidence it appears that the difficulty is most often encountered when too large a proportion of fine sand is used. The finer the sand the greater will be the amount of colloids adsorbed in the upper few

(*Courtesy Alvord, Burdick & Howson*)

FIG. 30.—Exterior View of Water-treatment Plant.

inches. These adsorbed colloids then set to a gel, extrude water and contract, compacting and cementing the sand grains. It is also true that the greater the amount of colloids present the greater would be the amount adsorbed so that with some waters a coarser sand will be required than with others.

Mud Balls. Under some conditions the sand in a filter shows a tendency to roll up into balls instead of separating into individual grains during the backwashing. Wolman and Powell[9] suggested that the cause might be the same as for shrinking or cracking and their suggestion seems plausible. Mud balls have been especially trouble-

[6] *Eng. News-Rec.*, **85**, 210.
[7] *Ibid.* **85**, 1081.
[8] *Ibid.* **92**, 1094.
[9] *Loc. cit.*

some where algæ have gotten past the sedimentation basin onto the filters. These gelatinous organisms are peculiarly effective in gumming up the sand. A microscopic examination of some mud balls from a filter treating Lake Michigan water showed them to be composed of sand grains cemented by diatoms. Mahlie [10] found that mud balls at Fort Worth, Texas, contained 20 percent of loose material which could be removed by washing and decanting, and about 37 percent moisture. The sand in the balls had an effective size of 0.50 mm. and a uniformity coefficient of 1.4. There was no marked variation between the material in large and small balls. The flocculent material removed by washing showed: ignition loss, 31.5 percent; SiO_2 30.0 percent; R_2O_3 29 percent; CaO 8.0 percent; MgO 2.3 percent. The larger balls are foul at the center due to anaërobic decomposition of the organic matter. Such conditions can be remedied when severe by treating the bed with a reagent which will peptize the gel acting as a binder or one which will cause the gel to shrink further until it draws away from the sand grains. Caustic soda has been known to accomplish the former and acid the latter.

Disinfection.

As a final step in the process of water treatment the effluent from the filter is usually disinfected to remove completely the possibility of the survival of harmful bacteria. If properly operated, the coagulation and filtration processes should effectively purify the water but disinfection is so simple and inexpensive that it is very cheap insurance against possible failure of the preceding processes.

Three rather different methods of disinfection have been employed: (1) chemical disinfectants, (2) actinic rays (ultra violet) and (3) heat.

Chemical disinfectants are more generally used at present than the other two. Of the various known disinfectants those which have been proposed for use in water treatment are with one exception all strong oxidizing agents. A large number have been suggested from time to time but those which have found practical application are the following: chlorine, hypochlorites, chloramine, permanganate, ozone, and "excess lime."

Use of Chlorine.

Chlorine is now used almost universally especially in large installations. With the perfection of machines for feeding the gas direct to

[10] *J. Am. Water Works Assoc.* 14, 420.

the water it has largely displaced hypochlorite. These feeding devices are arranged to control the flow of chlorine into a small stream of water forming a strong solution which is then fed to the main flow of water; or the gas may be delivered directly into the main flow through diffusers. Various types are on the market, some hand-controlled and some automatically controlled. The problem of chlorine feed is made difficult by the fact that the gas is so exceedingly corrosive in the presence of moisture. Silver tubing and glass are used as far as possible. If the gas is fed so rapidly that it cannot take up enough heat from its surroundings to make up for its latent heat of vaporization it may freeze and its pressure will drop. Chlorine is slightly and not readily soluble in water so that in feeding large quantities a considerable volume of solution or a large area of diffusers is required. The solubility of chlorine is greatest at about 10° C. Below this point the hydrate is formed and separates out and above it the gas is less soluble. At 10° the solubility is approximately 0.9 percent by weight, it drops to 0.7 percent at 20° and to 0.53 percent at 30°; it is 0 at 100°.

The absorption of chlorine by water is not simply a solution process; the following reversible reaction takes place:

$$Cl_2 + H_2O \leftrightarrows HClO + H^+ + Cl^-. \qquad (1)$$

The equilibrium constant for this reaction has been determined by Jakowkin [11] to be as follows:

$$\frac{[HClO] \times [H^+] \times [Cl^-]}{[Cl_2]} = 0.0448 \text{ at } 25° \text{ C.}$$

In very dilute solutions the reaction goes almost completely to the right but several hours are required before equilibrium is reached. Since the disinfecting action is practically completed in fifteen minutes to half an hour the unhydrolyzed chlorine must play an important part.

Hypochlorous acid (HClO) is so weak an acid

$$\left(\frac{[H^+] \times [ClO^-]}{[HClO]} = 6.7 \times 10^{-10}\right)$$

that it does not ionize appreciably [12] in the presence of even so weak an acid as carbonic $\left(\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3 \times 10^{-7}\right)$. It may react with hydrogen ions to form chlorine (reaction (1) to the left) or it may decompose to form hydrogen chloride and oxygen. In the presence of reducing agents free oxygen is not formed but the reducing agent is oxidized.

[11] *Z. physik. Chem.* **29**, 613.
[12] Noyes & Wilson, *J. Am. Chem. Soc.* **44**, 1630.

Rideal [13] suggests that the oxidation is due to hypochlorous acid and not to ClO ion since the oxidation potential is lower in alkaline solution where considerable ClO is present than it is in acid solution where hypochlorous acid predominates. The disinfecting action is generally attributed to its oxidation although no direct experimental evidence seems to be available.

Besides oxidation there are three other probable reactions between chlorine and organic matter. It may add directly to an unsaturated compound thus: $R_2C = CR_2 + Cl_2 \rightarrow R_2C(Cl) - CR_2(Cl)$; it may substitute for hydrogen on a carbon atom thus: $RCH_3 + Cl_2 \rightarrow RCH_2Cl + HCl$; or it may substitute for hydrogen on nitrogen thus: $RNH_2 + Cl_2 \rightarrow RNHCl + HCl$. Any of these reactions might well be as effective as oxidation in disintegrating the bacterial cell. In fact it is known that gelatin and peptone are rendered insoluble by the action of chlorine or bromine and an analytical method has been based on this reaction.[14]

The amount of chlorine required for disinfection depends upon the amount of organic matter present. One tenth to five or six tenths of a part per million is the usual range in filtered water. Two parts per million will disinfect as bad a water as any one would think of drinking. Where treated sewage is to be disinfected 5 to 50 parts per million of chlorine have been used.

Hypochlorites.

The hypochlorite most commonly used is that of calcium, really the chloride-hypochlorite ($CaClOCl$) commonly called "bleaching powder." The commercial product is made by the reaction of chlorine with slaked lime.

$$Ca(OH)_2 + Cl_2 \leftrightarrows CaClOCl + H_2O$$

and naturally contains such small amounts of silica, iron and aluminum as would occur in the lime. A good grade of "bleach" should be dry and should contain 35 percent or more of available chlorine. It deteriorates rapidly in the presence of moisture and carbon dioxide, especially in warm climates, due to the formation of hypochlorous acid which in turn loses oxygen. The reactions are:

[13] *Chemistry Industry* **40**, R 64.
[14] Rideal, *Analyst* **22**, 228.

$2CaClOCl + 2H_2CO_3 \rightleftarrows CaCl_2 + Ca(HCO_3)_2 + 2HClO$ and, as mentioned above, $2HClO \rightleftarrows 2HCl + O_2$. Carbonic acid as previously stated is more strongly ionized than hypochlorous acid.

In some cases this decomposition has resulted in the formation of enough oxygen to cause the containers to explode with some violence. Gill[15] attributes this to a catalytic effect of iron and manganese oxide on the decomposition of calcium hypochlorite and chlorate.

When a dolomitic lime (one containing magnesium) is used for the production of "bleach," magnesium chloride is formed. Since this is a very hygroscopic substance the absorption of moisture by the bleach is increased and it is therefore less stable than if made from a pure calcium lime. The addition of 20 percent of quicklime tends to stabilize bleaching powder.[16]

The reactions of hypochlorous acid with organic matter appear to be the same as those of chlorine. The addition and substitution reactions require the formation of chlorine by the reversal of reaction **(1)**. The fact that when chlorine is used it is available immediately as such probably explains its greater efficiency as compared with "bleach." Calcium hypochlorite is not very soluble (0.5 percent) and is ordinarily fed as a 1 or 2 percent suspension.

Sodium hypochlorite (NaClO) is more soluble and more stable and is sometimes used for convenience especially for small installations. It may be prepared by treating bleach with sodium carbonate; by treating sodium hydroxide with chlorine; or by electrolysis of sodium chloride.[17]

The question has been raised as to whether the formula of hypochlorous acid is HClO or HOCl. Since it decomposes to form either oxygen or chlorine it seems probable that both forms exist in equilibrium thus $H : \ddot{Cl} : \ddot{O} : \leftrightarrows : \ddot{Cl} : \ddot{O} : H$.

It is interesting to note in this connection that the bonding pairs of electrons are only slightly displaced toward the chlorine hence the non-polar character of the compound. In hydrogen chloride or sodium chloride the bonding pair of electrons is drawn in strongly to the chlorine and these compounds are strongly polar or ionizing but they are not oxidizing agents.

[15] *Ind. Eng. Chem.* **16**, 577.
[16] Aumonium and Elliot, *Abstracts Bact.* **8**, 70.
[17] Payne, *Chem. & Met. Eng.* **31**, 334.

Chloramine.

A number of investigators [18] have observed that the presence of ammonia and nitrogenous organic compounds increased the bactericidal action of chlorine. This has been attributed to the formation of chloramine (NH_2Cl) according to the reaction

$$Cl_2 + NH_3 \leftrightarrows NH_2Cl + HCl.$$

The chemical reactions between chlorine and ammonia have been extensively studied by Noyes and co-workers [19] and by Bray and Dowell [20] who showed that in dilute solution chloramine was formed according to the reaction given above. Under different conditions nitrogen and nitrogen chloride (NCl_3) may be formed. Raschig [21] has also shown that chloramine may be formed by the action of hypochlorite on ammonia. The chlorine in chloramine is in a similar state to that in hypochlorous acid, that is, it is an oxidizing and chlorinating agent. Its greater effect on bacteria has been accounted for on the supposition that it is more soluble than chlorine and penetrates the bacterial cell more easily. It does not decompose spontaneously as does hypochlorous acid and therefore its entire strength is available for disinfection.

Ozone.

The production of ozone (O_3) by a high tension discharge has long been known and it is also common knowledge that ozone is a

[18] Dakin, H. D., et al. "The Antiseptic Action of Substances of the Chloroamine Group." *Proc. Roy. Soc.* (London) B. **89,** B 614, 232-251 (1916).
De Berard, H. I., "Chloroamine at Denver Solves Aftergrowth Problem," *Eng. News-Rec.* **79,** 210 (1917).
Race, Joseph. "The Use of Ammonia in the Chlorination of Water," *Surveyor* **49,** 253 (1916).
Race, J., "Water Sterilization by Means of Chloroamine," *Eng. Contr.* **47,** 251 (1917).
Race, J., "Chlorination and Chloroamine," *Eng. News-Rec.* **78,** 6 (1917), also *J. Am. Water Works Assoc.* **5,** 63 (1918).
Rideal, Samuel. "The Influence of Ammonia and Organic Nitrogenous Compounds on Chlorine Disinfection," *J. Roy. Sanit. Inst.* **31,** 33 (1910).
Harold, Major C. H. H., "Further Investigation into the Sterilization of Water by Chlorine and Some of its Compounds," *J. Roy. Army Med. Corps* **45,** 190-207 (1925); *Public Health Eng. Abstracts,* **H-472,** 54 (1925).
Harold, Major C. H. H. and Ward, Capt. A. R., R.A.M.C., "Report on Experimental Work Carried out at the Army School of Hygiene to Demonstrate that Chlorine Gas in Association with Ammonia Gas is a More Efficient Sterilizer of Water than Chlorine Gas Used Alone or Chloris or Bleaching Powder," *J. Roy. Army Med. Corps* **42,** 414-23 (1924), and **43,** 19-23 (1924).
Public Health Eng. Absts. **J-942,** 89 (1924).
Monfort and Barnes, *Ill. State Water Survey Bull.* 16, p. 218.

[19] *J. Am. Chem. Soc.* **23,** 460; **42,** 2167; **42,** 2173.

[20] *J. Am. Chem. Soc.* **39,** 907.

[21] *Chem. Ztg.* **31,** 926.

strong oxidizing agent. It has been tried as a disinfecting agent in water and results in general confirm its bactericidal properties. Difficulty was experienced in early experiments in constructing a machine which would stand up under daily use. Ozone treatment has not been adopted for large installations in this country although a number are in use abroad. Costs are reported as being rather high. In a recent paper Rashkovich [22] describes a test of an ozonizer on filtered river water. Slow sand filter effluent required 4 to 5 parts per million using air of a minimum content of 2 grains per cubic meter and 15 minutes' contact. Water treated by coagulation and rapid sand filtration required 1.5-2 ppm.

One of the oxygens of the ozone molecule is available for energetic oxidation, while the other two behave like ordinary gaseous oxygen which is not an active oxidizing nor disinfecting agent.

Ultraviolet Rays.

The harmful effect of short wave radiations (400 μμ and less) on living cells is well known, as is the mercury lamp or arc for producing these radiations. The use of these rays for sterilizing water involves the use of a sufficient number of lamps so that the water may be exposed to their radiations in a thin film or layer. Turbidity and color, especially the brown color of water, are opaque to the short wave length rays so that it is necessary to clarify the water thoroughly before exposure. Pure water is reported to be transparent to ultraviolet rays to a depth of 10 cm.[23]

Coblentz and Fulton [24] have investigated the relative germicidal power in different portions of the ultraviolet spectrum and find that it is not characteristic of any one portion but extends from the very short or Schuman rays up to and including a length of 365 millimicrons. The effectiveness varies inversely with the wave length.

There seem to be two explanations of this action of ultraviolet rays. One is based upon the fact that these rays are known to produce detectable traces of ozone and hydrogen peroxide in aërated water and holds that the action is due to the oxidizing effect of these compounds on bacteria. The amounts of these oxidizing substances appear to be so small that it would seem more probable that there is a direct photochemical effect upon the bacterial cell material analogous perhaps to the action of actinic rays on silver salts or to the more familiar but unpleasant effect on the skin, sunburn.

[22] *Trans. Int. Conf. San. Eng.* 1924.
[23] Duclaux and Jeantet, *Compt. Rend.* **181**, 630.
[24] *Bur. Standards, Sci. Paper,* 495.

The advantage claimed for both ozone and ultraviolet systems is the absence of disagreeable reaction products or by-products. The machines seem to lack the sturdiness required of large installations and the costs appear to be high.

Excess Lime.

The coagulation which results when lime is added to hard water produces a considerable removal of bacteria in case the water is polluted. The addition of a grain per gallon in excess of that required for softening has been found by Sir Alexander Houston [25] to produce practically complete sterility. The treatment is applied before filtration and the water allowed to settle. It is then mixed with sufficient hard unpolluted water to neutralize the excess lime. A recent investigation of the process has been made in this country.[26] A pH of 9.5 was found necessary for bactericidal action and pH 10.0 to 10.3 was found more effective.

Miscellaneous Chemicals.

Potassium permanganate, iodine, bromine, "Chloramine T" (toluolsulfochloroamide), silver fluoride, and various other substances have been used in water disinfection for treating small quantities, for trips in the field, expeditions, etc., and of course boiling is always an effective though expensive and troublesome method especially if much water is to be treated.

The Disinfection Reaction.

The disinfection reaction has been shown by Chick [27] to be an orderly time process and the mortality to be a logarithmic function of time represented by the equation $\frac{1}{t} \log \frac{N}{N-X} = K$. This was interpreted to indicate that the reaction was monomolecular since the equation for the rate of reaction is of the same mathematical form as that for a reaction where only one kind of molecule is involved. The similarity of the equations is really little more than a coincidence. Noyes and Whitney [28] have shown that the expression for the rate of diffusion also has the same mathematical form.

The monomolecular equation is developed from the mass law which in turn is based on the assumption of a homogeneous system. Since

[25] *Repts. Met. Water Board* (London), also *Eng. Contr.* 62, 821.
[26] Scott and McClure, *J. Am. Water Works Assoc.* **12**, 598 (1924).
[27] *Rept. 8th Int. Cong. Appl. Chem.* **26**, 167.
[28] *Z. physik. Chem.*, **23**, 689.

bacteria are separated by an observable boundary from the liquid we must be dealing with a heterogeneous system. Nernst [29] states that it is useless to determine the order of a reaction in a heterogeneous system since the rate will be governed by the relatively slow process of diffusion and hence will appear to be of the monomolecular type or first order.

Nelson and Vosburgh [30] have also pointed out the inconsistency of considering enzyme reactions as monomolecular. It appears therefore that the rate at which bacteria are killed depends upon the rate at which the disinfectant diffuses into the cell or groups of cells.

Wolman [31] and Streeter [32] have shown an exponential relation to exist between the number of bacteria in the raw water and in the final effluent. The equation which has been found to fit a large number of cases is

$$E = CR^N.$$

Where E is the count in the final effluent, R is the count in the raw water and C and N are constants.

These theoretical discussions emphasize the fact that is frequently lost sight of, namely, that bacteria are not completely and immediately killed or removed by any disinfecting agent or mechanical process. The number killed or removed is a certain percentage of the number originally present, and if this number is sufficiently large then the number remaining after treatment will be large enough to be dangerous. In other words streams may become so heavily polluted that they cannot be used as water supplies with our present methods of treatment. Various agencies are at present working toward the determination of the maximum "load" which may be placed on filter plants.

The effect of increased temperature would be to increase the effectiveness of the disinfectant. There appears to be little data on the effect of temperature on the disinfection of water. Helger and Tietz [33] report no effect of temperature on the required chlorine dose within natural limits of temperature variation.

[29] *Ibid.* **47**, 52.
[30] *J. Am. Chem. Soc.* **34**, 790.
[31] *Am. J. Public Health* **11**, 1153.
[32] *J. Am. Water Works Assoc.* **9**, 157.
[33] *Gesundh. Ing.* **46**, 329.

Chapter XIII.

Odors and Tastes in Water.

Odors, unless precautions are taken in observation, may frequently be confused with tastes and tastes may be confused with odors so that the expression "tastes and odors" is frequently heard in reference to conditions where only odors really exist. Psychologists apparently recognize only four taste sensations at the present time. They are: sweet, bitter, sour and salt. All other "tastes" may be referred to odors which reach the nose at the time the material is tasted or to the sense of touch which, of course, is possessed by the tongue.

Certain waters undoubtedly possess tastes in the strictest sense of the term. Highly mineralized waters are salty and sometimes bitter. Swamp water may contain a bitter extract from leaves and grass. Acid waters, mine waters for example, are sour and some waters may have extracted a sweetish substance in their course. These true tastes are less frequent and troublesome than the so-called "tastes and odors" which are really odors. A bitter taste is the most common true taste in water supplies and where it exists it is usually associated with some odor. In view of these facts we shall direct attention to odors primarily.

Classification of Odors.

The classification of odors most generally accepted is that of the great Swedish naturalist Linnaeus modified somewhat by Zwaardemaker. This classification gives nine classes of odors. The wording below is that of Tichener:[1]

1. Ethereal or Fruit Odours.—All fruit and wine odours; the scents of the various ethers; the smell of beeswax.
2. Aromatic or Spice Odours.—All spicy smells; camphor turpentine, cloves, ginger, pepper, bay leaves, cinnamon, caraway, anise, peppermint, lavender, bitter almonds, rosemary, sassafras; thyme, geranium, bergamot; rosewood, cedar-wood, etc.
3. Fragrant or Flower Odours.—All flower scents; vanilla, tonka bean, tea, hay; gum benzoin, etc.

[1] *Textbook of Psychology*, p. 111.

4. Ambrosiac or Musky Odours.—Musk, ambergris, sandalwood, patchouli.
5. Alliaceous or Leek Odours.—Onion, garlic, asafœtida; india-rubber, dried fish, chlorine, iodine.
6. Empyreaumatic or Burned Odours.—Roasted coffee, toast, tobacco smoke, tar, burned horn, carbolic acid, naphthalene, benzine, creosote.
7. Hircine or Rank Odours.—Stale cheese, sweat, valerian, root and stem of barberry and black currant, lactic acid, caproic acid.
8. Virulent and Foul Odours.—Opium, laudanum, French marigold, fresh coriander seeds, bed bugs, squash bugs.
9. Nauseous Odours.—Carrion flowers, stinkhorn, water from wilted flower stems, decaying animal matter, fæces.

Zwaardemaker [2] points out that odors are due to the presence of certain chemical groups in the molecule of the aromatic substances. These groups he calls "odoriphores." The principal odoriphores are: esters, aldehydes, ketones, ethers, alcohols, acids, nitrites, nitriles, terpenes, pinenes, sulfides, arsenides, cacodyls, halogens, pyridine and pyrrole.

It is interesting to note that these odoriphores, especially those which are associated with the more pronounced and penetrating odors are unsaturated or reducing substances and would therefore be easily destroyed by oxidizing agents.

Whipple [3] gives the following classification of odors in water:

a — aromatic
C — free chlorine
d — disagreeable
e — earthy
f — fishy
g — grassy
m — moldy
M — musty
p — peaty
s — sweetish
S — hydrogen sulfide
v — vegetable

Psychologists do not have sufficiently refined analytical methods to permit of a definite qualitative classification of odors similar to that of colors. It is also probable that new odors will be produced from

[2] *Intern. Crit. Tables* **1**, 358.
[3] The Observation of Odor as an Essential Part of Water Analysis, *Public Health Papers and Reports, Am. Public Health Assoc.* **25**, 587-93 (1899).

time to time. The classification of Linnaeus and Zwaardemaker appears to cover present experiences fairly satisfactorily and since it has been adopted by International Critical Tables is to be recommended. The classification of Whipple if rearranged could be easily made to fit the International Critical Tables standard.

Quantitative Expression of Odor.

The usual method of expressing odor intensity in water depends largely on experience and memory and is relative.[4]

The accepted quantitative unit[5] is the *olfacty*. It is defined as the threshold or minimum number of molecules per cubic centimeter required to give a perceptible odor. This unit is obtained from the experimental data by dividing the minimum perceptible grams per cubic centimeter by the molecular weight of the substance and multiplying by 6.06×10^{23} (the number of molecules in a gram molecule or mol).

The olfactys of some common substances, quoted from the International Critical Tables, are: ethyl alcohol, 30×10^{12}; benzene, 41×10^{10}; phenol, 26×10^{10}; cresol, 50×10^{9}; pyridine, 31×10^{8}; iodoform, 42×10^{7}; scatole 17×10^{6}.

Odors in Water.

Next to pathogenic bacteria, odor-producing compounds are the most objectionable substances with which the water treatment plant operator has to deal. Odors are far more troublesome and cause quicker and more insistent complaints than either turbidity or color.

The sources of odors we may divide into two classes, natural and artificial. The natural sources of odors are those which are present and which would be present without the intervention of man. For convenience the natural odors may be further divided into two classes: those which commonly occur in surface supplies and those which occur in ground water. The natural odors in surface supplies are produced by either micro-organisms or dead organic matter.

Many micro-organisms (protozoa and algæ) produce essential oils which have an odor characteristic of the organism producing them. They are analogous to the perfumes or disagreeable odors of the higher plants and animals. A detailed discussion of the odors produced by micro-organisms is given by Whipple.[6] Table 21 furnishes a partial summary of the subject.

[4] Whipple, *opus cit.*
[5] *Intern. Crit. Tables* **1**, 358.
[6] *Microscopy of Drinking Water.*

TABLE 21.—*Odors Produced in Water by Micro-organisms.**

Group	Organism	Natural Odor
Aromatic Odor	Diatomaceae	
	Asterionella	Aromatic, geranium, fishy
	Cyclotella	Faintly aromatic
	Diatoma	Faintly aromatic
	Meridion	Aromatic
	Tabellaria	Aromatic
	Protozoa	
	Cryptomonas	Candied violets
	Mallomonas	Aromatic, violets, fishy
Grassy Odor	Cyanophyceae	
	Anabaena	Grassy and moldy, green corn, nasturtiums, etc.
	Rivularia	Grassy and moldy
	Clathrocystis	Sweet, grassy
	Coelosphaerium	Sweet, grassy
	Aphanizomenon	Grassy
Fishy Odor	Chlorophyceae	
	Volvox	Fishy
	Eudorina	Faintly fishy
	Pandorina	Faintly fishy
	Dictyosphaerium	Faintly fishy
	Protozoa	
	Uroglena	Fishy and oily
	Synura	Ripe cucumbers, bitter and spicy taste
	Dinobryon	Fishy, like rockweed
	Bursaria	Irish moss, salt marsh, fishy
	Peridinium	Fishy, like clamshells
	Glenodinium	Fishy

* Whipple, *Microscopy of Drinking Water*, p. 197.

The odors produced by dead organic matter may be due to soluble compounds in the cells which are leached out through long standing in contact with the water. The presence of swamps on the watershed is favorable for the development of these odors. They are usually associated with high color and a bitter taste. Such odors are generally described as woody or grassy.

The decomposition of organic matter will also produce odors especially when under anaërobic conditions. Such odors are due to the formation of sulfur compounds, nitrogenous compounds, etc., and are distinctly offensive. Where the organic matter is largely cellulosic in character the odor of decaying wood predominates.

The natural odors in ground water supplies are due principally to the presence of hydrogen sulfide or sulfur dioxide formed or occurring in the water-bearing stratum or in some stratum through which the water has passed. Such waters are frequently highly mineralized and

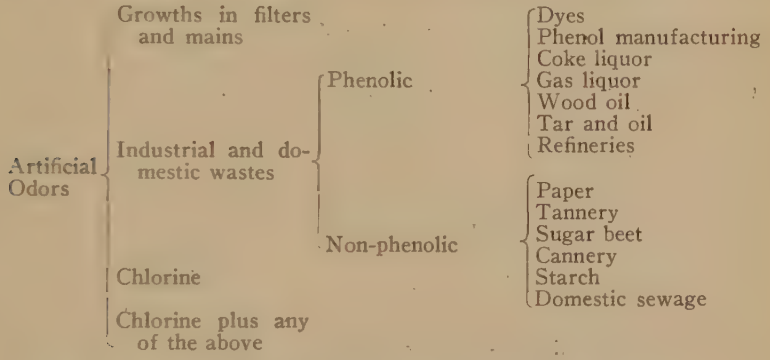
are avoided for municipal use unless there is no other supply available.

One or two cases have come under the writer's observation in which a small amount of natural oil occurs in the rock from which the water is drawn. The odor and tastes resulting from this condition are very disagreeable as can well be imagined.

In iron-bearing waters there is a characteristic bitter salty taste usually described as "irony." The taste in some cases at least is due to the ferric rather than ferrous compounds since it is not apparent when the water is first pumped but develops after aëration and standing.

Artificial Sources of Odors.

The artificial sources of odors may be classified as follows:



The effect of growths in filters and distribution mains is to produce odors similar to those of the microbial growths mentioned above.

Odors produced by industrial and domestic wastes have been extensively studied. Those produced by phenolic compounds are by far the most serious because they are detectable in such high dilutions. Gas oil odor is reported as being detectable in dilutions of 1 part in 5 millions.[7] Since nearly every town or city of any size has its gas plant, troubles from this source are becoming fairly general.

Some of the nonphenolic wastes carry aromatic substances; the cymene in sulfite pulp liquor is an example. In any case they are likely to cause anaërobic conditions during decomposition with the resulting production of putrefactive odors.[8]

The odor produced by chlorine used in disinfection is characteristic and disagreeable. There is considerable disagreement as to the amount of chlorine which can be detected. In many cases more than 0.2 to

[7] *Eng. Rec.* **58**, 434.

[8] *Pub. Wks.* **48**, 184; *Eng. News-Rec.* **87**, 771; Waring, *J. Am. Water Works Assoc.* **10**, 75.

0.3 ppm. above the amount required to react with the organic matter in the water is noticeable. It is difficult in some cases to distinguish between the true chlorine odor and the odor of chlorinated organic matter so that observations on natural waters may not refer to the true chlorine odor. Bartow and Warren [9] report that chlorine in distilled water was not detectable up to 3 ppm. This appears to be a rather high figure. The presence of ammonia appears to greatly reduce the chlorine odor due to the formation of chloramine.

The chlorine odor is not nearly as serious as the odors produced by the action of chlorine on organic matter. These appear to be of two types, the "iodoform" odor produced by the action of chlorine on phenolic substances, and a sort of woody or rank grassy odor caused by the action of chlorine on nonphenolic organic matter.

The odors produced by the introduction of phenols into water which is later disinfected by chlorination have caused serious trouble in a number of large cities. The chlorinated compounds formed are detectable in from 1 part in 500 million [10] to 1 in 750 million.[11] Kohman reports the spoilage of canned peas and pears from the use of chlorinated water contaminated by a 500 ton per day gas plant 6.5 miles above the intake in a stream having a flow of over 500 cubic feet per second.

The reaction between chlorine and phenols in such high dilutions is not entirely clear. Kohman found that none of the chlorophenols could be detected in dilutions of more than 1 to 100 million but that phenol diluted 1 to 750 million and then chlorinated was definitely noticeable.

Little seems to be known concerning the reactions involved with nonphenolic organic substances. It is well known that when such reactions occur substances of pronounced odor are produced. Observations on this point include troubles caused by the chlorination of water containing growths of Crenothrix,[12] sulfite liquor, Synura [13] and a variety of other products.

Methods of Treatment.

Aëration has been found generally successful in removing odors. It is particularly advantageous when the odors are due to anaërobic

[9] *J. Am. Water Works Assoc.* **11**, 881.
[10] Dieterle, *Gas Age* **46**, 427.
[11] Kohman, *Ind. Eng. Chem.* **15**, 518.
[12] Bushnell, *J. Am. Water Works Assoc.* **13**, 635.
[13] Hale, *ibid.*, **10**, 835.

decomposition of organic matter or to hydrogen sulfide or sulfur dioxide in well waters. As noted above, most of the odoriphore groups are easily oxidized and decomposed, many of them by mere aëration. Compounds with a pronounced odor must necessarily be volatile, and aëration allows them to escape.

Coagulation and filtration remove odors to a marked degree, the odors being removed with other organic matter. The petroleum odor

(Courtesy International Filter Co.)

FIG. 31.—Weleetka, Okla., Filter Plant Sedimentation Basin and Aërator.

mentioned above was completely removed by the floc formed when the water was softened for industrial use.

Probably the most generally successful and most easily applicable method of treating odors from both phenolic and nonphenolic organic matter is overchlorination. Hale found that Synura odors were destroyed and the organism killed when the chlorine dose was increased from 0.3 ppm. to 0.6-0.75 ppm. Similar results were obtained under

the writer's observation with odors from the same organism. Bushnell found that 0.3 ppm. of chlorine increases the odor due to crenothrix but 0.6 ppm. destroyed the odor. Kohman found that the chlorophenol odors were destroyed by a slight excess of chlorine and the writer has had a similar experience with wood oil wastes. Houston [14] recommends overchlorination followed by dechlorination. It appears therefore that overchlorination is rather generally applicable in the treatment of odors in water.

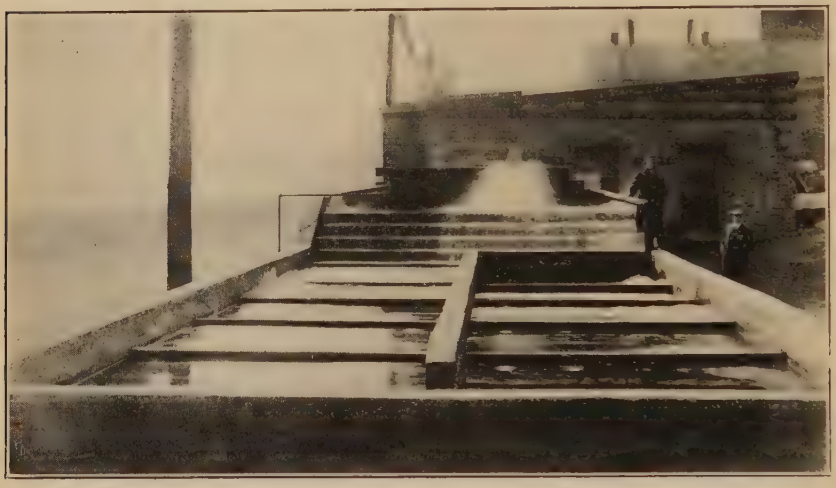


FIG. 32.—Aërator, Joliet, Ill.

Potassium permanganate (0.2 to 1.0 ppm.) has been used successfully by Houston in England as has ammonium persulfate and sodium persulfate. All three of these have also been used satisfactorily at Los Angeles.[15] These chemicals are rather more expensive than chlorine.

Odors due to an excess of chlorine may be overcome by treatment with any of the well-known "antichlors" after disinfection is complete. Sodium thiosulfate, sodium sulfite, sulfur dioxide and ammonia have all been used with success.

Preventive measures with respect to microörganisms have already been discussed. Other preventive methods will be found in the section on the treatment of sewage and trade wastes.

[14] *Surveyor* **68**, 43, 66.
[15] *Eng. Contr.* **62**, 60.

Chapter XIV.

Chemical Characteristics of Sewage.

Definition of Sewage.

Sewage may be briefly and broadly defined as "water-carried wastes." A more explicit definition given by the Committee of the Sanitary Engineering Section of the American Public Health Association[1] is the following:

(1) Wash water and water-carried animal, culinary and in some cases industrial wastes. (2) Liquid waste containing human excreta, ordinarily flowing in or from a house drainage system or sewer. "Excreta" includes, feces, urine, secretions from the skin, expectoration, etc. (3) Liquid wastes from dwellings and institutions, stables, and business buildings. It may also contain liquid wastes from industries. (4) A combination of (a) the liquid wastes conducted away from residences, business buildings and institutions and (b) from industrial establishments, with (c) such ground surface and storm water as may be admitted to or find its way into the sewers. (5) The ordinary liquid contents of a sewer containing organic wastes, which may or may not include street wash.

Constituents of Sewage.

Containing as it does body wastes (excreta), household wastes, community wastes (street washings, etc.) and, in manufacturing cities, the byproducts of industry, the combined waste liquor carries a very complex mixture of chemical substances. These substances may be of animal, vegetable or mineral origin. The animal or vegetable substances, "organic matter" will be found to include considerable material from all three of the principal biochemical groups, that is, the fats, carbohydrates and proteins as well as many decomposition products of the members of these groups. The mineral or inorganic constituents include sand and clay as well as the common mineral salts found in the water supplies. They may also include acids, alkalis, and salts in high concentra-

[1] *Am. J. Pub. Health* **15**, 331.

tions as a result of the discharge of such substances from manufacturing plants.

Temporal Variation in Composition. Not only is there a wide difference between the composition of sewages from different communities but there is a great variation in the composition of sewage from a given city. During the middle of the night the liquor is very weak consisting in many cases of clean water from leaky connections, drainage, etc., while in the middle of the day it is thick and milky. The character of the wastes also varies with the day of the week. Sunday sewage is weak, Monday sewage is soapy, and so on. In short, the laboratory assay of sewage is a difficult matter. A large number of samples must be taken at different times for examination and the results interpreted with care.

Waste Liquors. Waste liquors from factories will eventually find their way into some stream or watercourse. To determine the effect which they will have on such watercourse and the uses to which the water may be put is the object of sewage analysis. The harmful effect of such liquors is twofold: they may infect public water supplies or bathing beaches with disease organisms, thereby causing epidemics, or they may produce a nuisance and damage aquatic life.

In some cases waste liquors contain actual poisons such as cyanide, phenols, salts of the heavy metals, etc., but their occurrence is sufficiently rare to warrant deferring their consideration to a later point.

Living Organisms in Sewage. The living organisms in sewage are naturally limited to unicellular forms, i.e., bacteria and protozoa, although spores and cysts of various higher forms are present. In this group the variety of organisms is almost as great as the variety of chemical substances present. The presence of acids, alkalis or certain salts from manufacturing wastes may produce a practically sterile sewage. Straight domestic sewage will contain large numbers of intestinal organisms and wastes from the so-called "fermentation industries," a very wide group, including some dairying processes, some tanning processes, commercial solvents, etc., will each carry characteristic fauna and flora.

The prevention of disease can only be accomplished by disinfection and, as was stated in the discussion of water purification, the most economical point for the application of the disinfectant is in the water treatment plant rather than in the sewage treatment plant.

The numbers of bacteria added to a stream by sewage have been determined by the United States Public Health Service. Hoskins [2]

[2] *U. S. Pub. Health Rept.* **41**, 319.

gives the figures shown in Table 22 on the sewage from several American cities.

TABLE 22.—*Seasonal Changes in Number of Bacteria Added to Streams by Sewered Populations of Chicago and Peoria, Ill., Cincinnati, Ohio, and Louisville, Ky.*

	Billions of bacteria per capita per day		
	Growing on		
	Gelatin at 20° C. for 48 hours	Agar at 37° C. for 24 hours	B. Coli
Chicago:			
Summer	24 828	25 652	428
Winter	4 257	847	42
Year	15 296	11 171	230
Peoria:			
Summer	15 773	25 640	231
Winter	2 126	7 646	141
Year	11 054	19 313	187
Cincinnati:			
Summer	14 102	18 314	583
Winter	2 588	1 022	119
Year	11 770	12 256	358
Louisville:			
Summer	13 564	15 842	291
Winter	7 359	907	193
Year	10 841	7 962	222
Averages:			
Summer	17 067	21 362	383
Winter	4 083	2 600	124
Year	12 240	12 676	249

Consumption of Oxygen by Sewage.

Nuisance results from the putrefactive decomposition of organic matter. This decomposition produces substances which quickly consume the dissolved oxygen in the water, after which hydrogen sulfide, mercaptans and many other foul-smelling compounds are observed.

The depletion of oxygen causes the death by suffocation of practically all of the higher animals such as fish. The consumption of oxygen by sewage is called the "biochemical oxygen demand" and may be determined in the laboratory by diluting the sewage with a known amount of aërated pure water of known oxygen content and determining the oxygen consumed during the incubation of the diluted sewage for a definite time at a definite temperature. (This method will be found described in detail in the Standard Methods for Examination of Water and Sewage of the American Public Health Association.)

Besides the depletion of oxygen by putrefaction or biochemical action purely chemical reactions may occur which consume oxygen,

for example oxidation of ferrous sulfate from pickle liquors or sulfite from pulp mills. When such substances are discharged into streams they are frequently more harmful to aquatic life than organic wastes partly because the consumption of oxygen is very rapid and partly because they frequently cause an increase in acidity.

Nitrogenous Compounds in Sewage-Analysis.

While the most important characteristic of a sewage or waste liquor is its oxygen-consuming power, more data are available in the literature on the amount and character of nitrogenous compounds in wastes than on their oxygen demand.

Neave and Buswell [3] have recently discussed the composition of nitrogenous compounds in sewage as follows:

> *Free Ammonia.* Free ammonia is perhaps the oldest of the nitrogen methods in sanitary analysis. As an end-product in the bacterial metabolism of nitrogenous compounds, ammonia determinations may signify remote pollution of a water by organic matter. In sewage, similarly, free ammonia indicates the extent to which bacterial hydrolysis has proceeded. The difficulties in accurately determining ammonia by distillation have been appreciated. Mallet (*Annual Report of National Board of Health,* Appendix **D,** 1882) in 1881 pointed out that: "In the case of waters containing urea, and also other amidated bodies such as leucine and tyrosine occurring among the products of putrefactive decay, some ammonia is so easily formed from these substances by boiling with sodium carbonate, or even without this addition, that it is impossible to distinguish sharply between pre-existing "free" ammonia (of ammonium salts), and that formed by the action of alkaline permanganate, the so-called "albuminoid ammonia." More recently Phelps,[4] in a paper before the Laboratory Section of the American Public Health Association (1903), gave experimental data on the "free ammonia" of such substances as urea, gelatine, casein, egg albumin and peptone, showing that in all cases a few percent of the nitrogen was liberated during distillation. Since the presence of sodium carbonate seems to promote these hydrolyses, various attempts [5] have been made to substitute a milder alkali, such as magnesia, in its stead.
>
> Direct nesslerization following copper sulfate clarification of course obviates this decomposition, but for the most accurate work nesslerization is an uncertain procedure when dealing with a mixture like sewage. The present writers have successfully used aspiration of the ammonia into standard acid to avoid the defects of both the distillation and the direct nesslerization methods.

[3] *J. Am. Water Wks. Assoc.* **17,** 388.
[4] *J. Inf. Diseases,* **I,** 327-340 (1904).
[5] Davisson, B. S., *J. Ind. Eng. Chem.,* **10,** 600-6 (1918).

Albuminoid Ammonia. The albuminoid ammonia determination was proposed by Wanklyn, Chapman and Smith [6] as a measure of the unhydrolyzed, or only partially hydrolyzed, nitrogenous matter in a water sample. The digestion with alkaline potassium permanganate was thought at first to completely destroy such substances with a quantitative liberation of ammonia. Frankland and Armstrong [7] at that time were advocating their combustion method for carbon and the rivalry between the two methods brought to light some interesting defects in each. The great weakness of combustion processes, of course, is the preparation of a dry residue without loss of volatile components. It was carefully tested out by Mallet [8] in a long series of analyses and the precautions found to be necessary for reasonable accuracy exclude it from the class of routine methods. More recently Clark and Adams [9] have used the combustion process with some success in studying the carbon content of sewage.

The incomplete hydrolysis of urea during the permanganate digestion was recognized by Wanklyn,[10] but naively avoided by the statement that while pure urea was only partially decomposed, the impure urea of a sewage-polluted water showed no such resistance to hydrolysis. It was soon recognized, however, that the albuminoid ammonia nitrogen represented only a fraction of the total and various multiples of it have been adopted from time to time as measures of total nitrogen. Using a long series of known nitrogenous substances, Mallet [11] found the percent of nitrogen liberated to vary from zero to 95, with an average of 53. Even exhaustive treatment with alkaline permanganate, in some cases requiring several days, did not give complete recovery of nitrogen. He concludes: "The value of the results by this process depend more upon watching the process and rate of evolution of the ammonia than upon determining its total amount." Phelps also, in the report mentioned above, found wide variation in the recovery of ammonia from nitrogenous substances. In a series of sewage analyses, an average of 34.8 percent of the total nitrogen was liberated, though individual samples varied from 15.2 to 54.8 percent. The formula of Fuller

$$\text{Total Nitrogen} = \frac{12 \times \text{albuminoid } NH_3}{\text{Free } NH_3}$$

was thus shown to be in error in some cases by 25 percent.

Total Nitrogen. The Kjeldahl process for total organic nitrogen requires no discussion. It is subject merely to the error in the free ammonia when determined on the residue from the ammonia distillation. It would seem more desirable to determine total nitrogen by the Kjeldahl method and subtract free ammonia from it to give total organic nitrogen, since in this way the amine-nitrogen (which

[6] *J. Chem. Soc.* **5**, 445-54 (1867).
[7] *J. Chem. Soc.* **6**, 77-108 (1868); **14**, 825-50 (1876).
[8] *Annual Report of National Board of Health,* Appendix **D**, 1882.
[9] *J. Ind. Eng. Chem.*, **3**, 738-42 (1911).
[10] *J. Chem. Soc.* **5**, 591-5 (1867).
[11] *Loc. cit.*

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may be high in an effluent from anaërobic processes) is included in the total.

Interpretation of Analytical Results.

The interpretation formerly placed upon these determinations in water analysis has been carried over into sewage practice. The bulk of the putrefactive material in sewage seems to be regarded as protein and protein derivatives. The free ammonia represents an end-product of bacterial decomposition; the albuminoid ammonia is attributed to peptones and amino acids; and the total organic nitrogen, as stated in Standard Methods,[12] "comprises the nitrogen equivalent of nitrogenous compounds in various stages of hydrolysis, from complicated proteins to amino acids." Assuming the validity of this interpretation, the nitrogen would be expected to represent the concentration of putrefactive material or oxygen-requiring organic matter in the sewage. Our data for a purely domestic sewage, however, do not support these views.

The total nitrogen in the sewage can be almost entirely accounted for in the excreta of the population. A tabulation of the constituents of the excreta, as shown in the physiological chemistry texts, reveals the following facts: over 90 percent of the nitrogen is excreted as urea, and urea in being hydrolyzed by bacteria to ammonia and carbon dioxide has no oxygen demand. Only about 9 percent of the excreted nitrogen is found in the feces, but associated with it is 97 percent of the total oxidizable excremental organic matter. In other words all but about 3 percent of the oxygen demand of the excreta is associated with only a small variable fraction of the total nitrogen. The oxygen demand for each component of the excreta has been obtained by calculating the weight of oxygen required to convert the component to ammonia, carbon dioxide and water after the method of Rideal. The oxygen required totals up to 97 grams per capita per day. The fact that this daily oxygen requirement compares favorably with statistical data obtained in stream pollution studies[13] is merely coincidence or a balancing of errors, since our calculations disregard the oxygen demand of soap, paper, and similar material in the sewage.

Realizing then that urea is the main nitrogenous component discharged into the sewer and that it is slowly broken down by bacteria into ammonia, the nitrogen figures can be more adequately interpreted. The free ammonia represents urea already decomposed plus a little chemically hydrolyzed during the distillation. Albuminoid ammonia represents further chemical hydrolysis of the urea; it is a notoriously indefinite determination and the explanation becomes evident when the many factors, such as rate of distillation, concentration of alkali used, etc., which influence the slow hydrolysis are taken into account. The total organic nitrogen of course represents

[12] Am. Pub. Health Assoc., *Standard Methods*, 6th Ed., p. 72 (1925).
[13] *U. S. Pub. Health Bull.* **143**, 77 (1924).

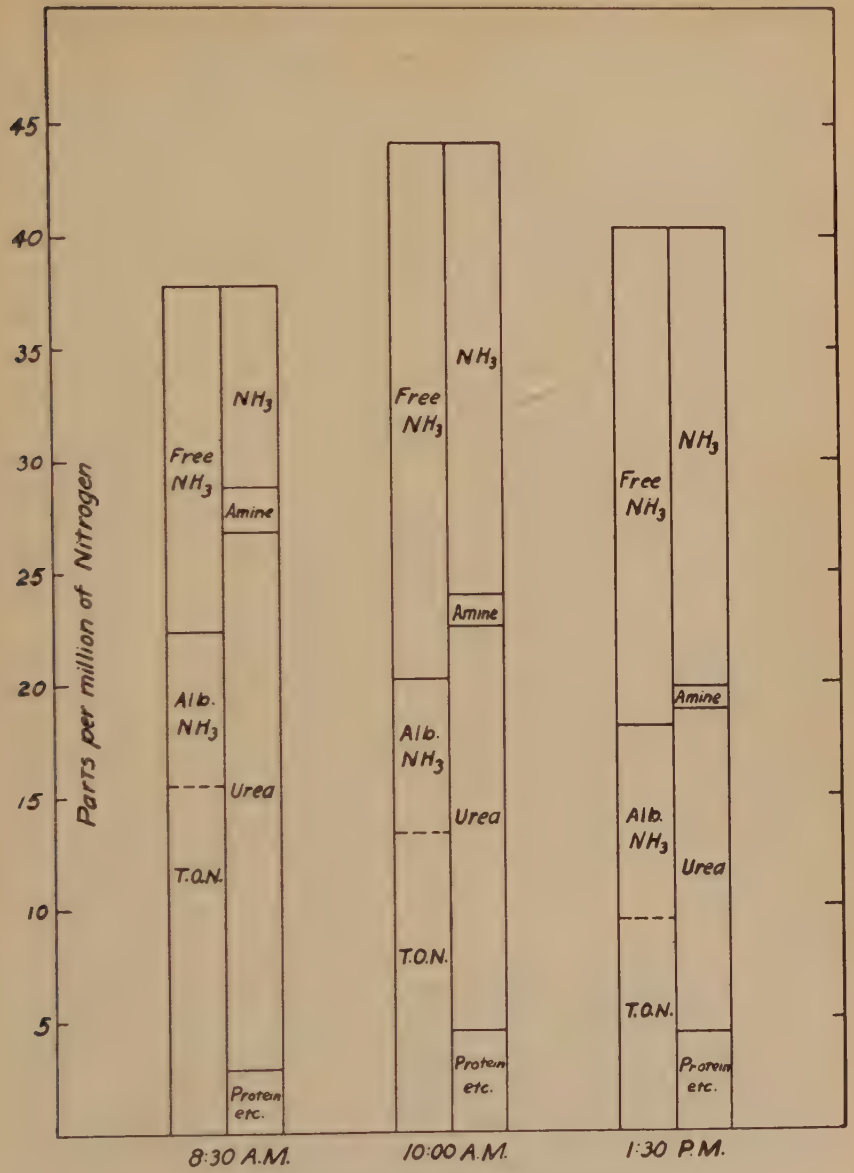


FIG. 33.—Forms of Nitrogen in Sewage.

total nitrogen minus the free ammonia and includes most of the urea.

To verify this interpretation we have analyzed a number of domestic sewage samples both by the routine methods and by determining the separate nitrogenous components of the sample using

the methods of the physiological chemist. Three such analyses are graphically represented in Figure 33. In each case the constituents are reported in parts per million of nitrogen. The so-called free ammonia is seen to consist of actual ammonia together with a small amount of amine (which is unimportant in the present discussion) and part of the urea. The albuminoid ammonia results mainly from destruction of some urea by the boiling alkali, though a very small amount also arises from certain compounds grouped together as the protein fraction. This protein fraction, being merely the difference between the total nitrogen and the sum of the components determined, includes not only the traces of other nitrogenous substances in the excreta but also nitrogen-containing material from the kitchen sink.

TABLE 23.—*Excretion by Normal Adult per Day.**

	Total weight	Content of				Oxygen required to oxidize excretion completely to CO_2, H_2O & NH_3
		Nitrogen	Carbon	Hydrogen	Oxygen	
Urine (1500 cc.):	Grams	Grams	Grams	Grams	Grams	Grams
Urea	35.	16.35	7.00	2.33	9.33	0.00
Creatinine	1.0	0.37	0.42	0.07	0.14	0.85
Uric Acid	0.75	0.25	0.27	0.02	0.21	0.21
Hippuric Acid	0.70	0.05	0.45	0.04	0.19	1.13
Ammonia	0.65	0.53	0.00	0.12	0.00	0.00
Thiocyanates	0.15	0.02	0.02	0.00	0.00	0.05
Oxy-acids	0.06	0.00	0.04	0.00+	0.02	0.11
Oxalic, Indican, etc.	traces	....	....	....	....	....
Mineral Ash	30.0	....	....	....	....	....
Totals	68.31	17.57	8.20	2.58	9.89	2.35
Feces (Dry basis)	20.00	1.80	26.80	4.07	6.66	94.25
Totals	98.31	19.37	35.00	6.65	16.55	96.60

*Compiled from Hawk's *Practical Physiological Chemistry* and Mathews' *Physiological Chemistry.*

It should be noted in this connection that in the nitrate determination, the predominance of urea introduces one error into the aluminium reduction method which deserves mention. As pointed out in *Standard Methods,* "during the long alkaline digestion some proteolysis may take place, giving high results"; it is, however, not so much a proteolysis as a hydrolysis of urea especially during the distillation of the resultant ammonia. For example, our Imhoff tank effluent has consistently shown a nitrate content of 0.2 to 2.0 ppm. over a period of six months, while the colorimetric method has shown no nitrate. Accordingly, whenever conditions permit, the colorimetric method would seem to be preferable to the reduction method.

To summarize, therefore, our analyses show, first that the main nitrogenous components of sewage are urea and ammonia; second,

that these components bear no constant relation to the oxidizable organic matter; third, that the albuminoid ammonia test, since it measures an indefinite portion of the urea, is worthless; and fourth, the free ammonia also includes some of the urea and is erroneous if the distillation process is used.

With the delicate analytical methods of the biochemist now at our disposal and the growing importance of river and lake pollution, there is an urgent need for the complete revision of our nitrogen determinations, with a view to either correcting their defects, or abandoning them in favor of more significant determinations.

Formula for Rating Sewage.

McGowan [14] some time ago suggested an empirical formula for rating sewages, which combined the nitrogenous matter with the value for the oxygen absorbed from potassium permanganate. His formula is:

Strength = Ammonia N + 4.5 (Organic N) + 6.5 (absorbed O_2).

The values used are expressed in parts per 100,000 and the oxygen determination varied from *Standard Methods of the A. P. H. A.* in that the $KMnO_4$ was one-eighth *N* instead of one-eightieth and the digestion was 4 hours at 80° F. instead of 30 minutes at 100° C.

On the basis of this formula a strong sewage is one which rates 175 units or more, an average sewage, 100-175, a medium 60-100 and a weak sewage is one which rates under 60. Because of differences in analytical methods and character of wastes this formula has not been extensively used in the United States. McGowan himself preferred to rate sewages on the amount of dissolved oxygen required to oxidize the organic matter ("biochemical oxygen demand") but since several days is required to carry out that test his formula was proposed as a substitute.

Data on Moscow Sewage.

Stroganoff [15] gives the data shown in Table 25 concerning the analysis of Moscow sewage expressed on a per capita basis. Since this sewage contains human wastes almost exclusively this author has discussed the data from the standpoint of the dietitian and finds that during prosperous times the nitrogen per capita corresponds to an adequate ration (2,200 cal.) but that during the war the nitrogen decreased to an amount equivalent to 1960 cal. per person per day as figured from the nitrogen. He also found that phosphorous pentoxide-nitrogen ratio in the sewage corresponded to that in the excreta of a

[14] *Royal Commission on Sewage Disposal, 5th Report,* Appendix **IV,** p. 1.

[15] *Report of the Commission of Investigation of Sewage Purification (1903-1922),* Moscow.

normal person (19.5 percent) during peace times but increased to a value indicating starvation (37 percent) during the war and the revolution. The nitrogen per capita per day is found to vary but little from 8 grams as judged by sewage analyses from various cities in Europe and the United States.

Typical British Sewage.

Table 24 serves to characterize British sewage in a general way:

TABLE 24.—*Typical Analyses of Crude British Sewage.**

	Parts per 100,000					
	a	b	c	d	e	f†
Free ammonia	7.31	4.43	5.0	10.61	16.58	2.3
Albuminoid ammonia	1.52	1.07	1.8	1.42	2.21	3.7
Oxygen absorbed in three minutes at 80° F.	....	3.51	12.8	5.30	9.50	50.7
Oxygen absorbed in four hours at 80° F.	17.81	13.99	24.0	19.81	21.19	69.2
Total solid matter	....	....	178.9	....	....	216.0
Chlorine	10.30	9.88	15.2	16.28	17.12	48.0
Nitrogen as nitrate	nil	nil	nil	nil	nil	nil
Suspended matter	17.6	46.5	86.0	49.50	62.1	40.0

* Purvis and Hodgson, *The Chemical Examination of Water, Sewage and Foods*, 2nd Edition.

† Sewage containing trade wastes.

Sewage of the United States.

Wagenhals, Theriault and Hommon [16] attach particular importance to the biochemical oxygen demand or the oxygen absorbed from permanganate and the suspended solids as a means of judging the character of a sewage. Tables 26 and 27 may be taken as representing the chemical character of sewage in the United States in those terms.

TABLE 26.—*Analyses of Raw Sewages in the United States.**

City	Oxygen consumed, 30 min. in boiling water	Suspended matter	Chlorine as chlorides	Ammonia nitrogen
	Ppm.	Ppm.	Ppm.	Ppm.
Chicago	38	141	40	8.8
Waterbury	46	105	48	7.8
Cleveland	50	252	246	12.0
Philadelphia	76	189	39	4.0
Akron	86	238	917	6.6
Columbus	93	215	65	11.0
Gloversville	95	406	158	12.0

* U. S. Pub. Health Service Bull. 132, *Sewage Treatment in the United States*, p. 118.

[16] *U. S. Public Health Service Bull.* 132.

TABLE 25.—*Composition of Moscow Sewage*, 1903-1922.*

Year	Population Served (Thousands)	Liters of sewage per capita per day	Analysis of sewage in grams per capita per day								
			Suspended Matter	Chlorine	Ammonia Nitrogen	Organic Nitrogen	Total Nitrogen	Oxygen Consumed ($KMnO_4$)	Organic Carbon	Phosphates	Sulfates
1903	361	93.5	63.0	14.3	8.2	0.8	9.1	3.7	...	1.8	8.5
1904	386	93.5	57.0	18.7	8.3	0.8	9.2	5.5	...	1.8	8.5
1905	425	99.6	62.0	19.5	8.2	0.8	9.0	5.7	...	2.0	6.1
1906	498	97.0	64.0	21.6	9.1	0.9	10.0	6.7	...	...	...
1907	525	96.0	64.0	17.4	8.1	0.8	8.9	5.4	...	...	...
1908	553	100.9	64.0	20.8	8.7	0.9	9.6	6.2	...	...	...
1909	585	102.0	52.0	17.8	8.3	0.8	9.1	6.9	...	...	...
1910	620	96.0	61.0	18.5	7.2	0.7	7.9	7.6	...	...	...
1911	660	84.9	56.0	17.7	6.7	0.7	7.4	7.6	...	...	...
1912	725	86.0	65.0	16.7	6.9	0.6	7.5	8.4	...	...	...
1913	840	86.0	57.0	15.9	7.2	0.7	7.8	8.4	...	...	...
1914	940	84.0	46.3	15.4	7.1	0.6	7.7	8.5	...	...	...
1915	960	92.4	50.1	13.1	8.1	0.8	8.9	8.7	...	...	...
1916	965	96.0	44.0	11.5	7.6	0.6	8.2	7.8	...	...	...
1917	950	97.0	32.7	10.9	6.4	0.5	6.9	6.4	...	...	...
1918	800	109.0	32.7	13.3	5.9	0.5	6.4	5.9	...	...	...
1919	725	124.0	37.8	13.5	5.9	0.5	6.4	6.6	...	...	...
1920	770	118.0	43.8	11.5	5.7	0.5	6.2	5.2	...	...	...
1921	930	110.0	36.7	9.7	5.1	0.8	5.9	4.8	4.5	1.9	4.8
1922	950	102.0	43.9	12.3	5.3	1.9	7.2	5.6	4.7	1.4	5.8

* Stroganoff, *Report of the Commission for Research Concerning Sewage Purification.*

TABLE 27.—*Composition of Raw Sewages in the United States (ppm).**

City	1-day oxygen demand	5-day oxygen demand	Oxygen consumed, 30 min. in boiling water	Suspended matter	Settleable solids, 2 hrs., cc. per liter	Ether soluble matter	Ammonia nitrogen	Suspended matter in supernatant	Chlorine as chlorides	Dissolved oxygen	Alkalinity as $CaCO_3$ by methyl orange
Atlanta (Peachtree)	15	52	35	226	2.5	83	..	..	86	0.0	68
Atlanta (Intrenchment)	25	63	35	106	2.4	104	..	..	93	.0	78
Rochester (Brighton)	22	67	24	101	2.0	16	..	18	45	3.7	178
San Marcos	32	67	29	110	2.2	18	15	10	83	2.8	306
Alliance	36	92	38	152	2.0	37	..	37	47	3.0	184
Rochester (Irondequoit)	45	104	39	188	2.1	34	..	50	82	.9	175
Houston (south side)	39	112	38	226	2.0	36	18	48	101	.8	304
Houston (north side)	52	116	45	200	2.5	39	17	46	136	.2	270
Reading	62	118	45	145	2.0	25	..	57	120	..	164
Baltimore	59	120	43	159	2.9	40	..	45	86	.2	136
Lexington	65	144	32	166	2.4	58	..	14	89	.1	196
Fitchburg	76	155	65	297	2.7	63	..	56	70	.3	97
Columbus	80	190	63	201	3.1	100	..	60	113	1.7	211
Sherman	57	202	64	254	5.0	69	26	85	129	2.5	415
Canton	118	213	61	261	5.3	62	..	62	79	.5	342
Average	52	121	45	187	2.7	52	19	45	90	1.2	208

* *U. S. Pub. Health Service Bull.* 132, p. 116.

A more recent publication [17] summarizes the data on the chemical characteristics of domestic sewage as follows:

> Ratios of Constituents to Sewered Population.—During recent years a number of different observers have made long-continued studies of the volume and composition of the combined sewage (i.e. sanitary sewage and storm water) from various sewered urban areas of known population. Such studies of the sewage from residential communities, where industrial wastes are a small item, have furnished a basis for calculating the ratio between the number of people contributing to a sewerage system and the average daily discharge of wastes in terms of the weights of such constituents, and indices are ordinarily determined in the physical and chemical examination of sewage. The ratios of sewered population to various sewage constituents as thus calculated have varied rather widely in different studies, and are probably at best of no great accuracy, so that there is no close agreement in standard references as to the average or model ratios. The estimates given in Table 31 are based upon data from a number of different sources and are considered to be fairly representative values for the combined sewage of American cities, exclusive of industrial wastes. It is recognized, however, that the element of personal judgment enters into any such summary, as the results depend largely on the choice of data.

TABLE 28.—*Average Composition of Domestic Combined Sewage, Exclusive of Major Trade Wastes.*

	Grams per capita per diem
Solids	
Total	439
Suspended	109
Dissolved	330
Volatile	182
Nitrogen	
Total	11.4
Free Ammonia	7.6
Oxygen consumed	51.5
Biological oxygen demand	100.0

In so far as these ratios—or any others which may be adopted in preference to them—may be considered as fair average values, they constitute a link between the observations made in a survey of sources of pollution and the observations made by direct examination of water as found in the river. They make it possible to convert data collected in terms of sewered population into terms of physical and chemical analysis, and thus to compare the amounts of various constituents actually found in the river with the amounts accounted for in the domestic sewage of all urban communities on the watershed above.

[17] *U. S. Pub. Health Bull.* 143, p. 77.

While such summaries are very useful, the wide variations of individual samples from average figures points to the need of better analytical methods. This need is frankly acknowledged by workers in sanitary chemistry and a considerable portion of the current research in this field is directed toward the improvement and development of laboratory tests.

TABLE 29.—*Average Analyses of 234 Samples of Screened Domestic Sewage, from May 3 to September 3.*[1]

	Maximum	Minimum	Average
Settleable solids (1 hr. Imhoff cone) per cent	0.47	0.13	0.26
Turbidity	447	129	237
Residue on evaporation ppm.	1560	840	997
Chlorides "	195	62	113
Alkalinity (Methyl Orange) "	493	237	420
Oxygen consumed (from $KMnO_4$ half hr. 100°) "	103	25	59.3
Free ammonia "	24.6	7.2	16.4
Albuminoid ammonia "	11.3	0.9	4.2
Total organic nitrogen "	40.0	4.0	12.3
Nitrate nitrogen "	14.6	0.1	1.4
Nitrite nitrogen "	0.59	0.0	0.15

[1] *Ill. State Water Survey Bull.* 18.

Chapter XV.

Methods of Sewage Disposal.

It is the purpose of this chapter to give a brief survey of sewage disposal and the various types of sewage treatment works merely as a necessary background for the discussion in following chapters on the chemistry of the processes involved. There are many excellent texts and reference books which treat fully the subject of the design and construction of such plants.[1] These have been consulted freely in the preparation of this summary.

Outline of Methods.

The term "sewage disposal" is frequently used where "sewage treatment" is really meant. This confusion of terms is unfortunate since each phrase has a definite and useful meaning. The methods of "sewage disposal" may be summarized as follows:

Sewage Disposal
- I. Without Treatment
  - a. Dilution
  - b. Irrigation
  - c. Fish ponds
- II. With Treatment
  - a. Screens { Bar / Fine
  - b. Sedimentation
    1. Grit chambers or detritus tanks
    2. Settling tanks
       - Plain { Septic { Dortmund / Separate Digestion { Alvord / With chemicals { Mechanical
       - Two-Story { Imhoff / Travis
  - c. "Filtration"
    1. Sprinkling { Rock / Clinker / Brush, etc.
    2. Contact beds
    3. Sand

[1] Metcalf and Eddy, *American Sewerage Practice*, McGraw-Hill; Babbitt, *Sewerage and Sewage Treatment*, Wiley & Sons; Kershaw, *Sewage Purification and Disposal*, Cambridge Public Health Series; Fuller, *Sewage Disposal*, McGraw-Hill; Imhoff, *Fortschritte der Abwasserreinigung*, Carl Heymanns Verlag, etc., etc.

d. Secondary tanks
e. Activated sludge [instead of (b, c. d)]
    1. Aeration
    2. Sedimentation
f. Special methods

Disposal Without Treatment.

Dilution.

It is obvious that if any material is uniformly dispersed in a sufficiently large amount of some neutral substance it will apparently disappear as far as ordinary methods of observation are able to discern. The amount of dilution necessary depends therefore on the accuracy of the observational methods employed.

In water standards a turbidity under 10 parts per million is not considered seriously objectionable. If sewage from a given source does not increase the turbidity by more than 10 parts per million, disposal by dilution would be considered satisfactory so far as turbidity is concerned. Similarly if the organic matter does not reduce the dissolved oxygen below the requirement of normal aquatic life, disposal by dilution may be considered successful from that standpoint.

It is just as essential that the matter carried by the sewage be uniformly dispersed as that the amount of diluting water be sufficient. Otherwise there will be local accumulations of sludge which will putrefy and cause nuisance and masses of unsightly floating solids will also be observable. There are few cases where coarse screens can be dispensed with and in most instances fine screens or sedimentation should be used prior to dilution. The consensus of opinion appears to be that where a flow of less than 2,000 to 3,000 gallons per capita per day is available for dilution, foul conditions are sure to result and that where the flow is more than 6,000 to 8,000 gallons per capita per day no nuisance results except from large floating objects and the formation of sludge banks.

The biological and chemical reactions occurring during the self-purification of streams are essentially similar to those taking place in the artificial treatment of sewage and will be discussed at a later point.

Broad Irrigation or Sewage Farming.

Broad irrigation or sewage farming has been rather extensively used in Europe and to some extent in this country in districts with low rainfall. Sewage is distributed over a given area of land by means of ditches and allowed to seep away. Where the soil is not of an open

texture the land is tiled. It is not possible to dose any one area continuously, several areas are dosed in rotation. The land is cultivated during the proper season of the year, thus taking advantage of the small manurial value of the sewage. In arid regions the sewage is of advantage for the water it furnishes. There is so strong a popular prejudice against the use of products raised on sewage farms in this country that their development is unlikely. The area required is so large that they are practically limited to small communities where sandy soil is available. Alvord, Burdick & Howson in their report on the Disposal of Chicago Sewage estimate that 93 square miles of land would be necessary to dispose of the sewage of the Sanitary District of Chicago.

Fish Ponds.

Fish, especially carp, are frequently found congregating about the mouth of a sewer or the outlet of a treatment plant, but only when the flow of the stream is sufficient to furnish the requisite amount of dissolved oxygen. Under proper biological control it is possible to dispose of sewage by running it into fish ponds. The process is by no means as simple as it might appear. The fish do not take up the organic matter directly but feed upon the smaller aquatic life which is stimulated by the sewage. It is a case of "big bugs have little bugs upon their back to bite 'em," etc. The proper relation between the various plants and animals must be maintained or the whole cycle will break down. The care required to maintain these fish ponds is so great that they would perhaps better be classified with artificial means of treatment. The area required is even greater than is necessary for broad irrigation.

Sewage Treatment.

The completeness of the treatment necessary for any given installation depends so much on local conditions and requirements, especially on such factors as the strength of the sewage and the volume of the body of water into which the effluent is to be discharged, that generalized statements regarding it cannot be made. A great variety of treatment devices are in use ranging in effectiveness from coarse bar screens which remove only large floating débris, to elaborate works turning out an effluent which would meet the drinking water standard so far as dangerous bacteria are concerned. A rather generalized and somewhat idealized flow sheet for complete treatment is given in Figure 34.

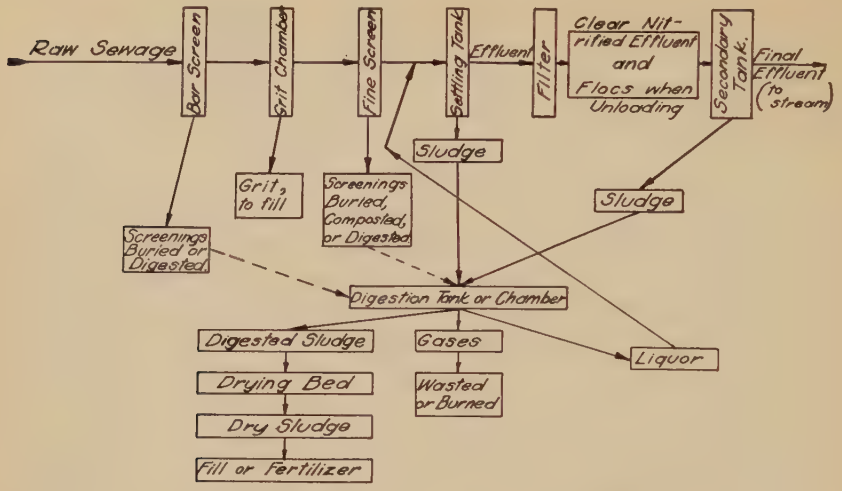


FIG. 34.—Complete Treatment of Raw Sewage.

Bar Screens.

The raw sewage passes first through screens made of bars spaced three-fourths of an inch or more apart. The bar screens are used primarily to catch pieces of boards and other large objects which would clog the channels or damage the pumps. They ordinarily catch a considerable amount of finer material in addition, such as paper, vegetable peeling and some feces. The amount of organic matter in these screenings is sufficiently large so that it cannot be spread out on the ground without breeding flies and causing a nuisance. It may be buried or composted or digested with the settleable solids if tank treatment is used.

The Grit Chamber.

The sewage next passes to the grit chamber where the velocity is decreased by increasing the cross-section of the channel so that coarse, heavy particles settle out. With a velocity of about 1 foot per second gravel, cinders and similar matter will be deposited, below this velocity coarser particles of organic matter will also be deposited. The proper adjustment of the velocity yields a sediment containing so little organic matter that it can be used for grading or fill without the danger of odors or nuisance.

Fine Screens.

From the grit chamber the sewage may be passed through "fine screens" or it may pass directly to the sedimentation tanks. Fine

screens usually have openings of one-quarter inch or less and are mechanically operated so that the screenings are continuously removed and the openings kept clear. A variety of types are in use including drum screens, belt screens and revolving disc screens. If the sewage contains a large amount of coarse floating matter such as vegetable hulls, matches, etc., screens will be found especially useful. They remove particles which would not settle out in the sedimentation tanks but which would produce scum and also clog the filter nozzles. In some cases where the available dilution is sufficiently large, screening may be sufficient treatment. A number of such installations are to be found in Germany.

The screenings are largely organic in nature and unless disposed of promptly will become very offensive. They may be drained and hauled away and buried or plowed into the soil, or the screenings may be mixed with the digesting sludge in the sedimentation tank and reduced with them.

Sedimentation.

The next step in the purification is sedimentation. This may be accomplished either with or without the aid of chemical coagulants and in tanks of various designs. The use of chemical coagulants, usually lime, lime with ferrous sulfate, or alum, is advantageous in certain trade wastes. For domestic sewage it does not appear to be regarded

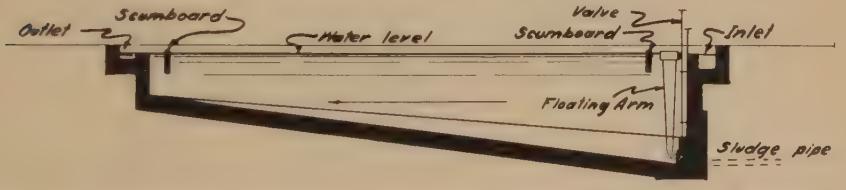


FIG. 35.—Diagrammatic Section of Rectangular Settling Tank (after Kershaw).

with favor at the present time because of the large amount of sludge which must be disposed of.

The tanks used for sedimentation may be of the following types:

Horizontal Flow Sedimentation Tanks. Such tanks are usually built from 6 to 10 feet deep, of such width that the velocity of flow will be less than the critical settling velocity of the settleable solids and of a total capacity to give the necessary detention period for sedimentation. They may be built deeper at the inlet end where the heaviest accumulation of sludge occurs and where the sludge is drawn off, or

the bottoms may be built hopper-shaped to facilitate sludge removal. When the plant is designed for separate digestion the sludge must be removed when fresh, every day or every few days, to avoid a nuisance.

Septic Tanks are designed with sufficient capacity to allow the accumulation and digestion of the sludge to take place in the sedimenta-

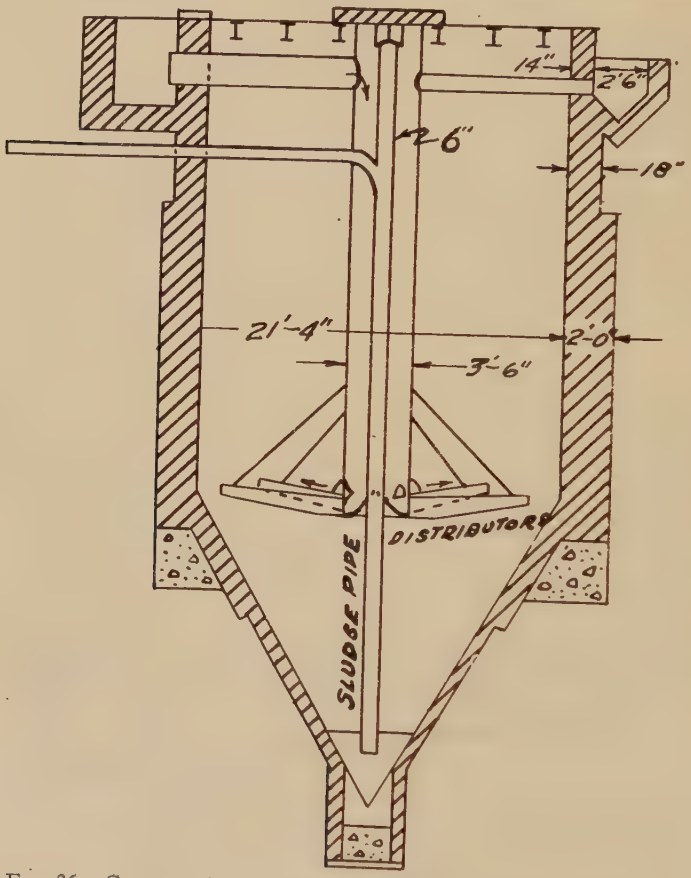


FIG. 36.—Cross-section of Dortmund Tank (after Kershaw).

tion chamber. Septic tank sludge is not removed until "ripe" or digested. The effluent from a septic tank is fouled by the products of the anaërobic digestion of the sludge.

Vertical Flow Tanks. In this type the sewage is introduced below the surface at the center of the tank and as low as possible without disturbing the sludge. The liquor passes upward leaving the settleable solids behind. The settling solids meeting the ascending liquor are

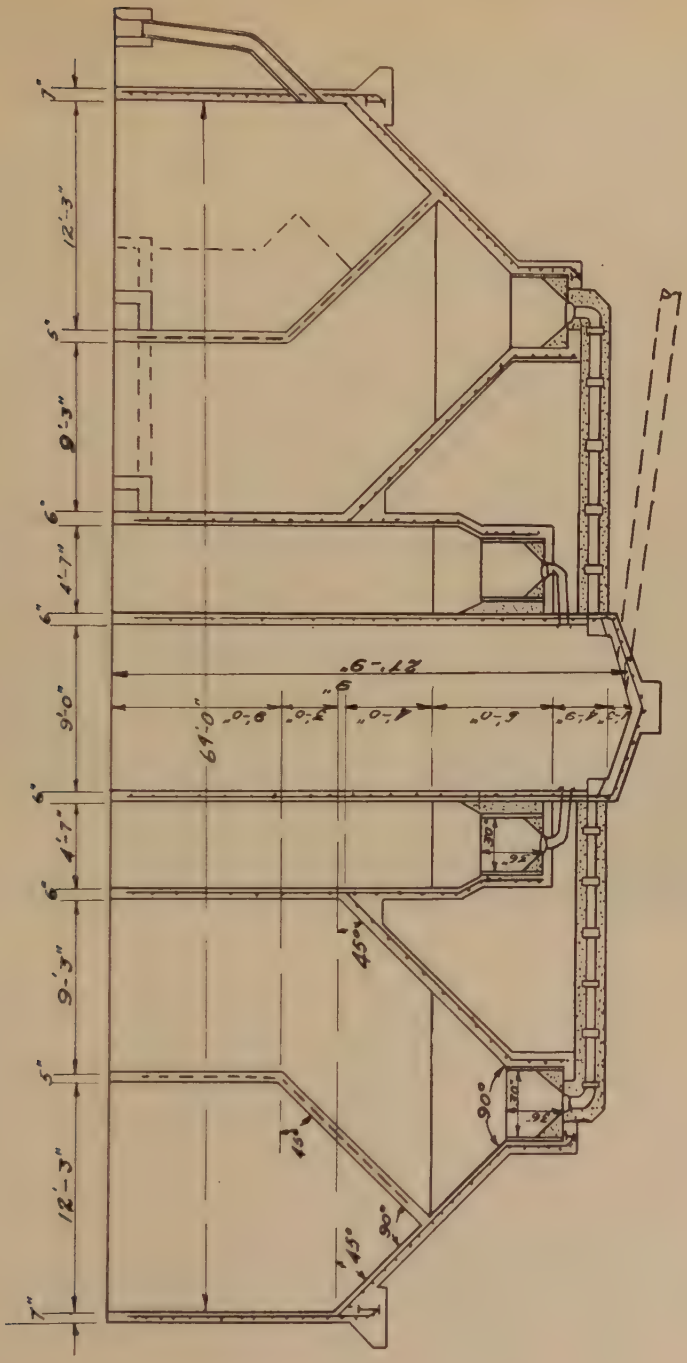


FIG. 37.—Cross-section of Travis Tank (after Kershaw).

said to adsorb some of the colloids in this type of tank although data we have seen fail to indicate the extent of this action. The *Dortmund* tank of this design was originally used with chemical coagulants and a number of lime soda water softeners operate on a similar principle. The sludge must be removed promptly to avoid disturbances due to putrefactive gases. (See Fig. 36.)

Mechanical Sludge Removal. Recently the use of mechanical devices to thicken and remove the fresh sludge has become very popular. They may be installed in either circular or rectangular tanks. Since they are automatic and continuous in their action they overcome the

FIG. 38.—Septic Tank, Urbana, Ill.

principal objection to plain sedimentation tanks, namely, the disagreeable laboriousness of removing the sludge from the sedimentation tank to the digestion tank. These mechanical thickeners also produce a sludge of lower moisture content than is obtained simply by sedimentation. Expensive steep sloping bottoms are not necessary in settling tanks equipped with such devices. A form in wide use is shown in Figure 39. The sludge is plowed toward the center of the tank by the revolving arms which rotate very slowly (once in 5 to 20 minutes approximately, depending upon the design). This plowing gently forces the liquor from between the sludge particles and delivers a very thick sludge to the center of the tank. The sludge is pumped from a sump in the center of the tank once or twice a day.

It will be noted that the sludge produced in all of the above tanks, except in the septic tank, is removed while still fresh and allowed to digest in a separate compartment. The septic tank as noted is merely

(*Courtesy Dorr Co.*)

FIG. 39.—Dorr Clarifier at Hartford, Wisconsin.

a sedimentation tank in which the sludge is allowed to accumulate and digest, being removed once or twice a year.

Two-story Tanks. The labor of handling the sludge and the disturbing effect of sludge digestion on sedimentation are both avoided

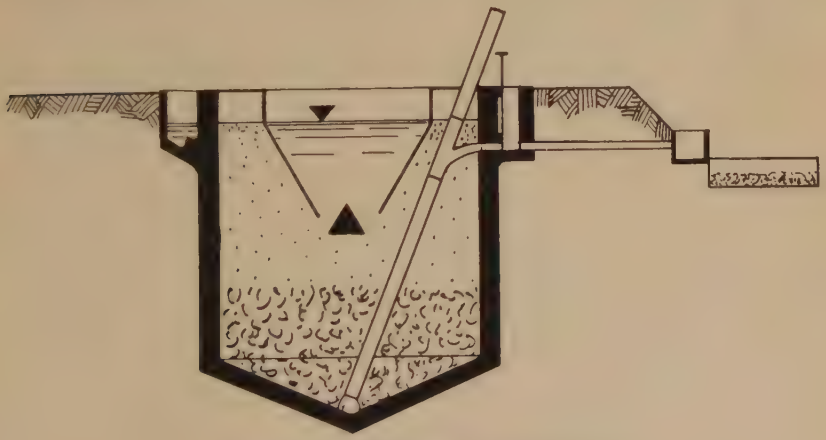


FIG. 40.—Cross-section of Imhoff Tank.

by the use of *two-story tanks.* These tanks are built with the sedimentation chamber over the sludge digestion chamber and communicating with the latter by means of a slot. The bottom of the sedimentation chamber is sloped toward the slot so that the sludge slides down

into the digestion chamber below. The Travis tank (*see* Fig. 37) was originally designed so that a portion (one-fourth to one-tenth) of the fresh sewage passed into the digestion chamber displacing the septic liquor which was discharged with the effluent from the sedimentation tank. This design has not been adopted in this country. Dr. Karl Imhoff of the Ruhrverband has designed a two-story tank commonly called the Imhoff or Emscher tank. (*See* Fig. 40.) The general construction is similar to the Travis tank but there are some important improvements. There is no outlet to the digestion chamber except for the drawing off of sludge and hence no flow of fresh sewage through the digestion chamber. The slots at the bottom of the sedimentation chamber are baffled to prevent gaseous products of digestion from rising through the sedimentation chamber thereby fouling the liquor and disturbing sedimentation. These tanks are usually built rather deep (25 feet or more) for the purpose of improving the quality of the sludge (see *Sludge Digestion*). Because the Imhoff tank requires comparatively little operating supervision and yields a sludge which dries easily on sand beds it has become very popular in this country.

Sedimentation if at all successfully carried out removes from 25 to 40 percent of the organic matter from the sewage, the effluent being milky or opalescent but free from settleable suspended matter.

Filtration.

If the body of water into which the sewage is to be discharged is not large enough to receive the settled effluent without damage it may be further purified by so-called *"filtration."* The results are obtained by contact of the effluent with microbial growths on the surface of the material of which the "filters" are made rather than by true filtration. This material may be gravel, crushed rock, clinker, coke, brush, etc. Where gravel, rock, clinker or coke is used it is usually screened to a fairly uniform size. The various sizes used range from quarter to half inch up to 2 or 3 inch or even larger. The finer material furnishes more surface per cubic foot but becomes clogged more readily and therefore requires more care.

The material is arranged in beds from 5 to 10 feet deep and is dosed from the top by means of troughs or sprinklers. The sprinkler is more commonly used, whence the name "sprinkling filter" which is generally applied to filters of this type. (*See* Fig. 41.) The dosage is intermittent, the cycle being determined by local conditions. The organic matter in the tank effluent, which is largely colloidal, is almost

completely removed in its passage through the filters, part of it being precipitated in the microbial jelly and part oxidized to carbon dioxide and nitrate. The effluent from the filters should be perfectly clear except for flocs of the microbial growth which break off and pass out of the filter. At times, especially in the spring and fall, this breaking off of flocs, called "unloading," is very extensive. These flocs settle readily and if desired may be removed in a "secondary" sedimentation tank. The effluent from the final tank should be clear and stable, that is, it should contain sufficient oxygen dissolved or as nitrate to oxidize any remaining organic matter.

(Courtesy Pacific Flush Tank Co.)

FIG. 41.—Sprinkler Filter.

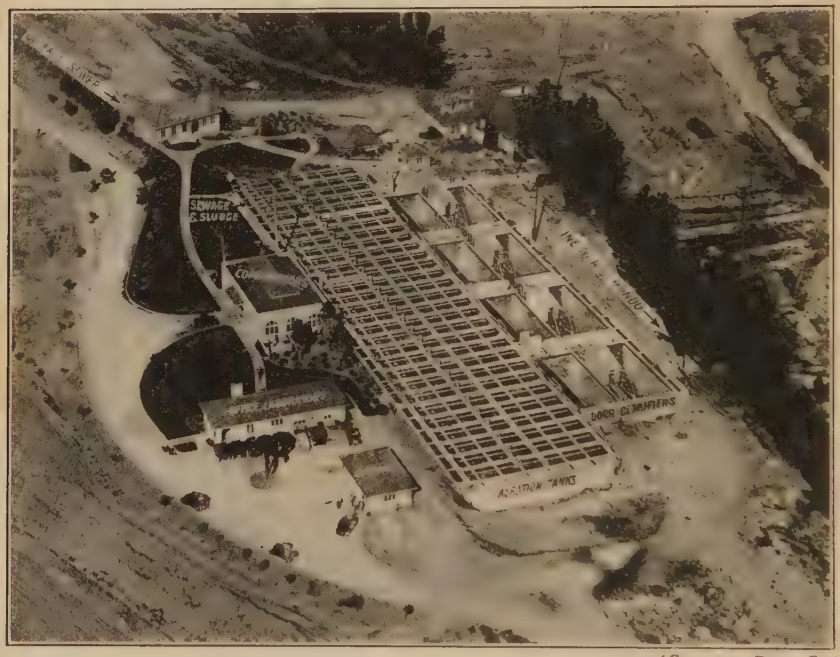
If the treated liquor is to be discharged near a bathing beach or a water supply it may be disinfected with chlorine.

When the hydrostatic head is not sufficient to operate sprinkler nozzles or where the settled effluent is stale and odors are to be avoided rock beds may be dosed by flooding from the bottom and then draining off after a period of contact. Such devices are known as "contact beds." Their action is similar to that of sprinkling filters but the results are inferior.

"Intermittent sand filters" operate much as do trickling or sprinkling filters. Because of the very fine grained material the top layer of sand must be cleaned frequently to prevent clogging. For the same reason they must be dosed at a relatively low rate so that they are practically limited to relatively small installations. When properly operated sand filters turn out a very high quality effluent.

Sludge Digestion.

The settled solids as already indicated are allowed to undergo a *digestive* or *rotting* process by which the less stable compounds are liquefied and decomposed. This action is brought about by various microörganisms commonly present in the sludge. The principal final products of this reaction are gases, notably carbon dioxide and methane, dissolved substances, and a black humus residue which has an earthy or tarry odor. This residue, the digested sludge, as drawn from the tanks carries 3 to 10 times its weight of water and is run out onto sand beds



(*Courtesy Dorr Co.*)

FIG. 42.—Activated Sludge Plant.

where the water readily drains away leaving an inoffensive residue of an earthy consistency. This material may be used for fill or for enriching poor soil.

The Activated Sludge Process.

The activated sludge process may be substituted for sprinkling filters or for both sedimentation and filters. Activated sludge consists of flocs

of microbial growth similar to that which is found on filter stone. This floc may be built up by blowing air through the sewage for a time, allowing it to settle, decanting and feeding with fresh sewage. In large plants operated on a continuous flow plan the sewage from the screens or from sedimentation tanks passes into an aëration chamber, where it meets a predetermined amount of activated sludge from the sedimentation of previously treated sewage and is stirred by compressed air introduced through porous plates. The floc as it comes in contact with the liquor under aërobic conditions acts much as it does in filters, taking up colloidal organic matter, part of which is used in the growth of the floc and part oxidized to carbon dioxide and nitrate. After the necessary aëration period (roughly two to six hours) the liquor passes to sedimentation tanks where the sludge settles and the clear liquor is discharged. The required amount of sludge is returned to the aëration chambers and the remainder is digested or pressed for fertilizer.

The area required for an activated sludge plant depends upon local factors, but is much less than that required for tanks and filters ($\frac{1}{10}$ to $\frac{1}{15}$). The first cost is also less but the operation cost is much higher.

A well operated activated sludge plant should give a somewhat better effluent than is obtained from trickling filters.

Summary of Sewage Disposal Methods.

The various means of sewage disposal are summarized in the following outline, which is given in a more abbreviated form in Figure 31.

Sewage Disposal Methods.[1]

A. Without Treatment
   1. Irrigation
   2. Dilution
B. With Treatment
   1. Separation of solids and liquids
      a. Coarse solids by racks
      b. Floating and coarse suspended solids by screens, scum boards or skimming chambers
      c. Grit, by grit chamber
      d. Settleable solids, by tanks
      e. Suspended solids, by
         (1) Sedimentation
         (2) Chemical precipitation
         (3) Flotation
         (4) Centrifuging
         (5) Sand filtration
      f. Colloids by precipitation or filtration
   2. Treatment of liquid
      a. Oxidation (Note: Some possible exceptions to this classification are noted in later chapters)

[1] *Am. J. Pub. Health* **15**, 334.

(1) Dilution
(2) Irrigation
(3) Sand filtration
(4) Contact bed
(5) Sprinkling filter
(6) Activation
(7) Direct oxidation with lime
(8) Miles acid process

b. Disinfection
(1) Liquid chlorine
(2) Bleach

c. Sterilization
(1) Heat
(2) Chemicals

3. Disposal of effluent
a. Irrigation
b. Dilution

4. Treatment of solids
a. Screenings and scum
(1) Burying
(2) Burning
(3) Composting

b. Grit—used as filling

c. Sludge
(1) Removed undigested as liquid
(a) Covered in furrows
(b) Lagooned
(c) Dumped at sea

(2) Digested
(a) In full stream of sewage, septic tank, biolytic tank
(b) In small amount of sewage, Travis tank
(c) Without sewage, Imhoff tank, separate digestion

(3) Removed, digested as liquid
(a) Covered in furrows
(b) Sprayed in fertilizer
(c) Lagooned
(d) Dumped at sea

(4) Concentrated (either digested or undigested)
(a) Sedimentation and decantation
(b) Mechanical thickeners

(5) Removed, concentrated as a liquid, then
(a) If undigested, treated as (1) or digested separately as in (2) (c) above
(b) If digested, treated in (3) above or dewatered as in (6) below

(6) De-watered to spadable condition
(a) Sand beds, draining and evaporation
(b) Pressing
(c) Centrifuging
(d) Exhausting, Oliver filter
(e) Wringing, between rollers

(7) Removed as cake or in spadable condition
(a) Dumped at sea
(b) Used as filling
(c) Used as fertilizer
(d) Mixed with fuel and burned

(8) Dried in a kiln by heat
(a) Used as fertilizer
(b) Used as fertilizer base.

Chapter XVI.

The Degradation of Organic Matter.

Oxidation and Reduction.

The fact that in nature organic matter undergoes slow oxidation has long been realized. It was discussed by Liebig in 1840[1] and was called "eremacausis" or slow burning. Carbon dioxide was recognized as the final product of this combustion although humus was known as a partial or intermediate result of the process.

The mechanisms of these biochemical oxidations and reductions are discussed at some length by Dakin.[2] Although the question is presented by Dakin from the standpoint of human and animal metabolism the conditions encountered are sufficiently similar to those met with when dealing with reactions produced by microörganisms so that the data have many direct applications in the chemistry of sewage treatment.

Oxidation does not necessitate the presence of oxygen. For example:

$$CO + H_2O \rightarrow HCOOH$$
$$HCOOH \rightarrow CO_2 + H_2.$$

Here carbon monoxide is oxidized to carbon dioxide in the absence of dissolved oxygen and with the formation of hydrogen.

Such reactions are aided by the presence of compounds which can combine with hydrogen, the so-called "hydrogen acceptors." Oxygen is the hydrogen acceptor in many cases but not in all. Where decomposition of organic matter occurs in the presence of molecular oxygen the oxidation appears to be brought about through the aid of certain substances which combine with oxygen to form peroxides (e.g., benzaldehyde). These peroxides then bring about the oxidation of substances which would not be attacked by molecular oxygen. The peroxide theory is supported by the fact that hydrogen peroxide produces oxidation results in vitro similar to those brought about by organisms.

[1] Liebig, Justus V., *Chemistry in its Application to Agriculture and Physiology*, 1st Ed. (1840).

[2] *Oxidations and Reductions in the Animal Body*, Longmans Green (1922).

Considerable interest has been aroused among biochemists in a derivative of cystine (glutamic acid + cystine) called glutathione. This compound which may be represented by the abbreviated formula RCH_2SH is easily oxidized as follows:

$$2RCH_2SH + \tfrac{1}{2}O_2 \rightarrow RCH_2S - SCH_2R + H_2O.$$

The oxidized form is in turn easily reduced;

$$RCH_2 - S - S - CH_2R + H_2 \rightarrow 2RCH_2SH.$$

The reduced substance is referred to as the "cysteine form" and the oxidized as the "cystine form." Dakin [3] summarizes the properties of cysteine and cystine as follows: "This pair of substances, readily interconvertible under conditions prevailing in the cell, possess precisely the properties which a co-ferment adapted to an oxidase system would be expected to possess, and as such they occupy thus far a unique position. The reduced (SH) form present in almost all living cells can take up molecular oxygen while the oxidized (S — S) form so produced can act as a hydrogen acceptor and so catalyze oxidation reactions of that type." Glutathione is widely distributed in nature, being found in both animal and vegetable cells. There is therefore strong presumptive evidence that it acts as a catalyst in biological oxidations and reductions. Considerable experimental evidence has also been accumulated to substantiate this assumption.

Reductions occur during the decomposition of organic matter as well as oxidations but little appears to be known concerning their mechanisms. One class of reducing reactions is well recognized, however: those in which oxidation and reduction occur simultaneously. For example two molecules of an aldehyde may react to give an acid and an alcohol.

$$2RCHO + H_2O \rightarrow RCH_2OH + RCOOH.$$

Decomposition of Fatty Acids.

The fatty acids resulting from the hydrolysis of the fats, appear to be completely oxidized in the body to carbon dioxide and water. According to the most generally accepted theory the oxidizing agent attacks the beta-carbon atom (second from the carboxyl group) forming the beta-hydroxy or beta-ketonic acid; e.g., stearic acid is oxidized as follows:

$$CH_3(CH_2)_{14}CH_2 . CH_2 . COOH \rightarrow CH_3(CH_2)_{14}CHOH . CH_2 . COOH \rightarrow CH_3(CH_2)_{14}CO . CH_2 . COOH.$$

[3] *Opus cit.*

The next step merely requires hydrolysis to form an acid with two less carbon atoms than stearic, namely, palmitic acid. This process is then repeated till the molecule is completely broken down.

Other reactions are known to occur in the degradation of fatty acids, such for example as the removal of hydrogen to form a double bond in the alpha or beta position.

Comparatively little appears to be known concerning the anaërobic decomposition of fats. At the present time there is very little information as to the extent to which fats are decomposed in sludge digestion.

Decomposition of Carbohydrates.

The various common carbohydrates are apparently all hydrolyzed to glucose in the first step of their decomposition.

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6.$$

From this point on, the oxidation in the animal body has been and is being extensively studied. The reactions appear to progress to the final end-products, carbon dioxide and water, by various paths, but it seems certain that glyceric aldehyde, methyl glyoxal, and lactic acid are among the intermediate products.

There are many conflicting statements in the literature on the anaërobic decomposition of carbohydrates and considerable work must be done before definite conclusions can be drawn. Cellulose is the most important carbohydrate found in sewage and there is some question whether it is extensively decomposed during sludge digestion. Certainly much unchanged cellulose material can be recognized in "ripe" sludge with the naked eye and with the microscope. The time recorded by investigators of cellulose fermentation is in most cases much longer than is allowed for sludge ripening.

Decomposition of Cellulose.

The earliest work on the decomposition of cellulose was done by Popoff in 1875 and by Hoppe-Seyler in 1883. Considerable work was done by Omeliansky (1895-1902) and more recently (1913) McBeth and Scales[4] have summarized the field of cellulose fermenters. The crude cellulose of perennial woody plants is attacked with considerable difficulty by bacteria. The tissue of annual plants yields much more readily to bacterial attack, and crude fibre which has been partially hydrolized by heating with dilute acid or alkali is easily fermented.

[4] U. S. Dept. Agric., *Bur. Plant Industry Bull.* 266.

TABLE 30.—*Products of the Commercial Fermentation of Cellulose.**

	Sulfite pulp	Sulfite pulp	Sulfite pulp	Sulfite pulp	Filter paper	Cellulose from megass	Rice straw cellulose	Cane sugar	Xylose from rice straw	Xylose from rice straw
	Percent									
Acetic acid	31.8	59.4	35.1	28.2	43.0	74.6	66.2	22.5	60.3	79.7
Butyric acid	...	...	28.6	...	...	...	...	...	...	...
Lactic acid	...	...	4.8	45.1	36.6	...	...	57.0	...	...
Alcohol	27.6	...	2.2	12.9	8.3	...	0.5	7.5	15.5	1.6
Carbon dioxide	42.4	49.5	...	...	...	27.8	47.5	...	...	28.1
Hydrogen	1.0	0.7	...	...	...	0.2	0.4	...	...	0.2
Methane	0.2	7.6	...	...	...	8.0	7.2	...	...	7.3
Total	103.0	117.2	...	...	...	110.6	121.8	...	...	116.9

* Lymn & Langwell, *J. Soc. Chem. Ind.* **42**, 282 T.

The decomposition of cellulose by bacteria when it does occur follows four different lines:[5]

1. Methane fermentation, produced by sewage bacteria (from sewer slime), giving methane, carbon dioxide and the lower fatty acids (formic to butyric acid).
2. Hydrogen fermentation, produced by *Bacterium fermentationis celluosæ* (Omeliansky), giving hydrogen, carbon dioxide and the same fatty acids as in (1).
3. Methane-hydrogen fermentation, produced by thermophilic bacteria of different kinds, leading to methane, hydrogen, carbon dioxide and formic and acetic acids.
4. Nitrogen fermentation, produced by denitrifying bacteria, that is, those assimilating nitrogen from the air or other sources, and yielding nitrogen and carbon dioxide.

A quantitative picture of the products of commercial fermentation of cellulose is given in Table 30 by Lymn & Langwell.[6] These authors submit the following equations for the formation of the products mentioned in the table, basing their assumptions on their own experience and the work of Neuberg on fermentation of sugar by yeast.

The first action is probably the hydration of cellulose and its breakdown to pyruvic acid and hydrogen. This is endothermic, so that pyruvic acid is not likely to be found as an end product.

$$C_6H_{10}O_5 + H_2O \rightarrow 2CH_3.CO.COOH + 2H_2 \qquad (1)$$

Under suitable conditions the pyruvic acid and hydrogen combine to give lactic acid

$$CH_3.CO.COOH + H_2 \rightarrow CH_3.CHOH.COOH \qquad (2)$$

This is an exothermic reaction and lactic acid is actually found in the products.

Under other conditions pyruvic acid splits off carbon dioxide to yield acetaldehyde.

$$CH_3.CO.COOH \rightarrow CH_3.CHO + CO_2. \qquad (3)$$

This is only faintly exothermic, so that aldehyde-fixing agents would be necessary to prevent further splitting of the aldehyde. The fixation of aldehyde is difficult with the cellulose fermentation, owing to its powerful reducing action, and has not yet been successfully accomplished.

The aldehyde may then, according to the conditions of fermentation, follow one or both of two courses; it may be reduced to alcohol as in (4), or hydrolyzed to a mixture of acetic acid and alcohol as in (5).

[5] Heuser, West & Esselen, *Textbook of Cellulose Chemistry*, p. 176 (1924).
[6] *J. Soc. Chem. Ind.* **42**, 282 T.

$$CH_3.CHO + H_2 \rightarrow CH_3.CH_2.OH. \quad (4)$$

$$2CH_3.CHO + H_2O \rightarrow CH_3.CH_2.OH + CH_3.COOH. \quad (5)$$

By again changing the conditions, the alcohol once formed may break down into a mixture of acetic acid and methane.

$$2CH_3.CH_2.OH \rightarrow CH_3.COOH + 2CH_4. \quad (6)$$

This change has been repeatedly observed and is sometimes difficult to prevent.

The high yields of acetic acid obtainable can only be explained by a reaction such as:

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_3.COOH. \quad (7)$$

A secondary reaction, well known in biological processes, results in the breakdown of lactic acid to butyric acid.

$$2CH_3.CHOH.COOH \rightarrow CH_3.CH_2.CH_2.COOH + 2CO_2 + 2H_2. \quad (8)$$

Finally, over-aëration results in complete oxidation of any of the above products to carbon dioxide and water.

It must be borne in mind that Lymn and Langwell are referring to the commercial fermentation of cellulose under controlled conditions. The course of the reactions in a sludge digestion chamber we can at present only conjecture.

Molds are known to attack cellulose but the products of the decomposition appear to have been studied but little. Some species are said to produce oxalic and citric acids.[7]

Hutchinson, Clayton and Richards[8] have reported an aërobic organism, *Spirochaeta cytophaga,* which when provided with the proper amount of nitrogen, preferably as an inorganic salt, will reduce straw and similar material to a humus in about three weeks.

Decomposition of Proteins.

The proteins which in the living cell are the nitrogenous organic compounds have undergone considerable decomposition by the time they reach the sewer. As mentioned in a previous chapter nitrogen in sewage is largely in the form of ammonia and urea (NH_2CONH_2). The undecomposed proteins are concentrated in the settled sludge and constitute a considerable percentage of it.

Native proteins are composed of a variety of amino acids of which the type formula is $RCHNH_2COOH$, where R is a more or less com-

[7] Russel, *Micro-organic Population of the Soil,* p. 133.
[8] *J. Agric. Sci.* **9,** 143, and *J. Min. Agric.* **28,** 398.

plex group. In many of the amino acids R is a relatively simple aliphatic or aromatic hydrocarbon but in others it may include carbohydrates, phosphoric acid, sulfur compounds and other complexes. In the natural protein the amino group of one amino acid is combined with carboxyl group of the next.

$$\begin{array}{l} RCH.COOH \\ | \\ NH_2 \end{array} + \begin{array}{l} RCH.COOH \\ | \\ NH_2 \end{array} \rightleftarrows \begin{array}{l} RCH.COOH \\ | \\ HN-C-CHR \\ \quad\; \| \quad\; | \\ \quad\; O \quad NH_2 \end{array} + H_2O$$

The number of amino acids thus combined to form casein, the protein of milk, has been estimated at from 60 to 130.

It will be noted that, reading the equation above from left to right, water is formed. The reverse reaction, the hydrolysis of the protein molecule into its component amino acids, is the first step in the decomposition of a protein and is brought about by enzymes or by heating with dilute acid or alkali. Bacteria do not appear to be able to hydrolyze natural proteins readily unless some of the simpler decomposition products are present to serve as food material while the reaction is starting.[9] Once the hydrolysis has occurred the amino acids are attacked with great ease by bacteria and a variety of products formed.

Dakin[10] summarizes the decomposition of amino acids by bacteria as follows:

I. $R.CH_2.CHNH_2.COOH + H_2 \rightarrow R.CH_2.CH_2.COOH + NH_3$ (Reduction)

II. $R.CH_2.CHNH_2.COOH + O_2 \rightarrow R.CH_2.COOH + NH_3 + CO_2$ (Oxidation)

III. $R.CH_2.CHNH_2.COOH + H_2O \rightarrow R.CH_2.CH_2.OH + NH_3 + CO_2$ (Hydrolysis)

IV. $R.CH_2.CHNH_2.COOH \rightarrow R.CH_2.CH_2NH_2 + CO_2$ (Amine formation)

V. $R.CH_2.COOH \rightarrow R.CH_3 + CO_2$ (Carboxylic acid decomposition)

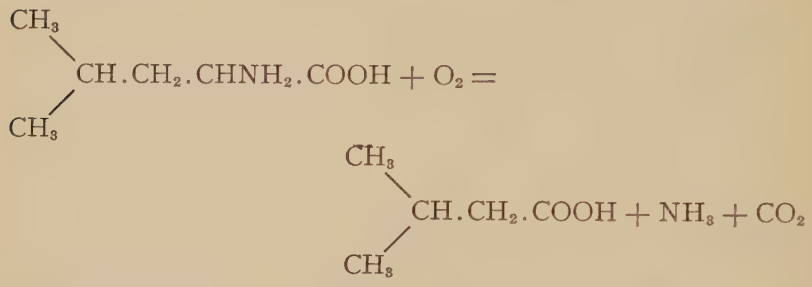
In general, it may be said that anaërobic bacteria are prone to *reduce* α-amino acids with formation of saturated fatty acids and liberation of ammonia (I). The formation of phenylpropionic acid from phenylalanine is an example of this type of change:

$$C_6H_5.CH_2.CHNH_2.COOH + H_2 = C_6H_5.CH_2.CH_2.COOH + NH_3$$

[9] Bainbridge, *J. Hyg.*, **11**, 341 (1911); Lomanitz, *Abstracts Bact.*, **8**, 9 (1924); Mito, *Acta Schol. Med.*, Kyoto, **1**, 433 (1917); Otsuka, *Ibid.*, **1**, 199 (1916); Sperry and Rettger, *J. Biol. Chem.*, **20**, 445 (1915); and Underhill, *Physiology of Amino Acids*, 1915, p. 36.

[10] *Opus cit.*, p. 98.

Aërobic bacteria more frequently *oxidize* the α amino acid to a fatty acid containing one fewer carbon atom, carbon dioxide and ammonia being set free (II). Thus leucine may be converted into isovaleric acid (Nencki):



Yeasts, on the other hand, have been shown by F. Ehrlich to convert the amino acids into alcohols, carbon dioxide and ammonia (III). Alanine, for example, yields ethyl alcohol:

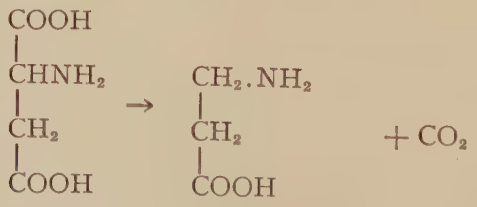
$$CH_3.CHNH_2.COOH + H_2O = CH_3.CH_2OH + NH_3 + CO_2$$

The net result of this last reaction indicates neither reductions nor oxidation but simply hydrolysis and liberation of carbon dioxide. It will be shown, however, that probably both oxidation and reduction are concerned in this change.

Another type of reaction (IV) very commonly effected by bacteria involves the liberation from the amino acid of carbon dioxide but not ammonia. Amines are formed in this way. Tyrosine, for example, yields p-hydroxyphenylethylamine:

$$OH.C_6H_4.CH_2.CHNH_2.COOH = OH.C_6H_4.CH_2.CH_2NH_2 + CO_2$$

Details concerning many of the bases thus found, some of which are of great physiological importance will be found in Barger's *Monograph on The Simpler Bases.* Carbon dioxide is also frequently liberated from the dicarboxylic acids such as aspartic and glutamic acids and from the acids produced by the oxidation of amino acids according to the second reaction (V). The formation of β-alanine and cresol from aspartic acid and tryosine respectively are examples of this type of change.



(*Aspartic acid*) (*β-Alanine*)

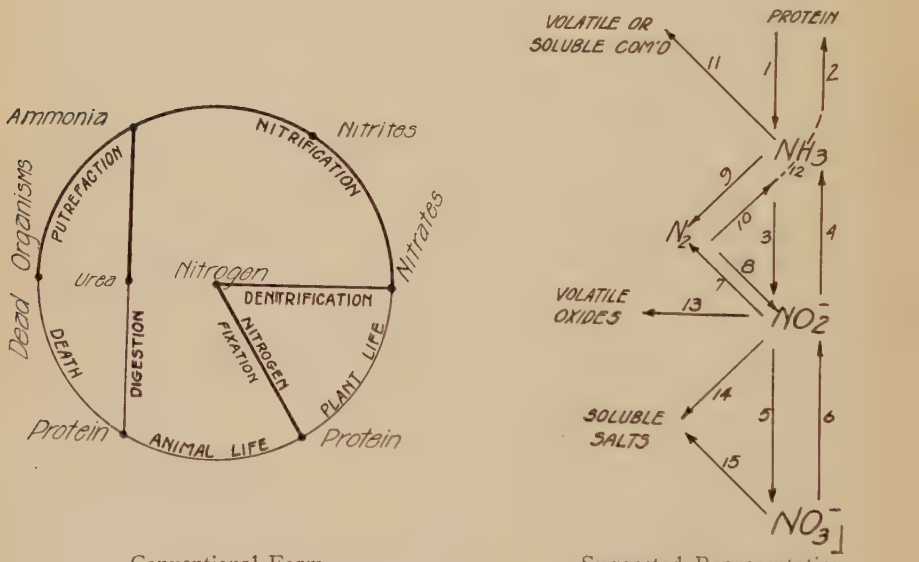
A combination of a number of these reactions may be effected by a single organism and different results may often be obtained using the same organism growing under varying conditions.

It appears then that ammonia, carbon dioxide, fatty acids, alcohols, amines and hydrocarbons may result from the bacterial decomposition of proteins. The fatty acids and alcohols may be further decomposed according to the reactions given in the previous paragraphs.

Chapter XVII.

The Nitrogen Cycle.

Because of the intimate relation between nitrogen compounds and the building up and breaking down processes of life (anabolism and catabolism) their reactions are sometimes represented diagrammatically as a cycle—the so-called "nitrogen cycle." The evidence for the occurrence or non-occurrence of the reactions of this "cycle" during



Conventional Form. Suggested Representation.

Fig. 43.—Nitrogen Cycle.

the process of sewage treatment have been summarized by Buswell and Neave.[1] The following discussion is based largely on this summary.

The conventional nitrogen cycle (Fig. 43) used in most text books on sanitary subjects emphasizes certain distinctions which are not of particular importance when applied to the reactions in sewage disposal. For instance, the change from vegetable to animal protein does not

[1] *Ill. State Water Survey Bull.* 18, p. 68.

materially affect the final decomposition reactions although it is represented by a large arc of the circle. The probable chemical course of some of the oxidation and reduction reactions is not brought out clearly by the diagram, nor is the reversibility of these reactions emphasized sufficiently for the purposes of the present discussions. Denitrification is represented as the direct reduction of nitrate to nitrogen, while undoubtedly nitrite and ammonia are formed as intermediate products. Nitrate is also represented as being transformed directly into plant protein while chemical evidence requires its preliminary reduction to ammonia. By including death in the circle the reactions are made to appear to take place in one direction only, i.e., clockwise, while in fact all of the reactions are reversible and must be so regarded in interpreting the bio-chemistry of sewage disposal. We suggest, therefore, representing the chemical reactions of the nitrogen cycle as shown at the right in Figure 43.

Ammonification.

If we begin with proteins at the top of the figure, we note first that these may be decomposed by means of hydrolysis to form ammonia. The intermediate steps have been worked out by Robinson.[2] Apparently amino acids are first formed and these may then be further broken down to ammonia, organic acids and carbon dioxide, according to one or more of the following reactions:

Reduction—$R.CH.NH_2.COOH + H_2 = R.CH_2COOH + NH_3$

Oxidation—$R.CH.NH_2.COOH + O_2 = RCOOH + CO_2 + NH_3$

Hydrolysis—(1[3]) $R.CH.NH_2.COOH + H_2O = RCH.OH.COOH + NH_3$

(2) $R.CH.NH_2.COOH + H_2O = RCH_2.OH + CO_2 + NH_3$

The reactions are undoubtedly the result of microbial activity. Marchal[4] attributed ammonification in the soil to the activity of the *B. mycoides* group and *B. fluorescens liq.* while Conn[5] claims that the Mycoides organisms are relatively poor ammonifiers and that two organisms *Ps. fluorescens* and *Ps. caudatus* which multiply rapidly in

[2] Robinson, R. H., and Tarter, H. V., "The decomposition of protein substances through the action of bacteria," *J. Biol. Chem.* **30**, 135

[3] Ehrlich, Paul, *Z. Ver. Rubenzucker-Ind.* 1905, 539-67.

[4] Marchal, Emile, "Sur la production de l'ammoniaque dans le Sol par les microbes," *Bull. Roy. Belgique*, 1893, (3) XXV, 727-71.

[5] Conn, H. J., Ammonification of manure in soils, *N. Y. Tech. Bull.* **67** (1919).

freshly manured soils are the important ammonifiers. Waksman [6] has shown that fungi, especially actinomycetes, are good ammonifiers. Doryland's investigation [7] of these reactions from the standpoint of energy requirement of the bacteria indicate that ammonia formation is incidental. The bacteria attack compounds from which they can obtain energy; if suitable non-nitrogenous compounds are present proteins will be attacked but slightly, or not at all, and consequently little or no ammonia will be formed.

Nitrification.

The fact that ammonia may be oxidized to nitrite and then to nitrate by *Nitrosomonas* and *Nitrobacter,* respectively, is a reaction well recognized by both soil chemists and sanitary chemists. It occurs during the final stages of aëration of the activated sludge process or during the passage of settled sewage through the various sewage filters. Since nitrification does not occur until most of the oxidizable organic matter has been removed, the presence of nitrates has frequently been taken as a measure of the degree of purification. In the soil calcium or magnesium carbonate and carbon dioxide seem to be essential to the reaction. Since these organisms are sensitive to changes in acidity it seems probable that the buffer effect of these carbonates may explain their beneficial action. No intermediate chemical products between ammonia and nitrite have been detected so that this step of the reaction is not definitely known.

Loss of Gaseous Nitrogen.

From purely chemical considerations there appear to be three ways in which the formation of nitrogen may be brought about. *First,* by the direct oxidation of ammonia, with the formation of nitrogen and water. This occurs when ammonia is burned in pure oxygen. A similar oxidation takes place when ammonia reacts with chlorine or bromine, in which case halogen acid and nitrogen are formed. *Second,* by the reduction of nitrates and nitrites by organic matter with the formation of nitrogen and carbon dioxide. When nitrates are reduced in the course of inorganic reactions, considerable amounts of ammonia

[6] Waksman, S. A., "Importance of mould action in the soil," *Soil Science,* 1918, VI, 137-55 (Bibliography); "Cultural studies of species of Actinomyces," *Ibid.,* 1919, VIII, 71-207; Waksman, S. A., and Curtis, R. E., "Actinomyces in soil," *Ibid.,* 1916, I, 99-134; 1918, VI, 309.

[7] Doryland, C. J. T., "The influence of energy material upon the relation of soil microörganisms to soluble plant food," *N. Dak. Agri. Expt. Sta. Bull.,* 1916, p. 116.

as well as various oxides of nitrogen are formed. *Third,* when nitrites and ammonia are both present "auto-oxidation reduction" may occur, one nitrogen atom oxidizing the other and itself being reduced according to the well known reaction $NH_4NO_2 \rightarrow N_2 + 2H_2O$.

Any of these courses of reaction might occur in nature. In the sewage beds studied by Chick [8] and Muntz and Laine [9] loss of nitrogen was said to have occurred under ample aëration, while in the experiments of Adeney,[10] the reaction was undoubtedly one of reduction.

The data on this phase of the nitrogen cycle are in many cases of a negative character. Experimenters have failed to show a balance of nitrogen, and where the difference was greater than could be otherwise accounted for, it was attributed to evolution of gaseous nitrogen. Russel refers to the works of Chick, Adeney, and Muntz and Laine for evidence of the occurrence of this specific reaction in sewage disposal. A review of the references, however, raises a question as to whether this reaction occurs to any such extent as is generally supposed. Chick, in her work on trickling filters,[11] does not take account of the nitrogen in the microbial growth on the filters. This is also true of the work of Frankland quoted by Adeney and Letts, and of that of Muntz and Laine. In the experiments of Adeney and Letts septic tank effluent was incubated with the addition of potassium nitrate. The incubation took place in tightly stoppered bottles. At the conclusion of the experiment the various forms of nitrogen, with the exception of the Kjeldahl nitrogen, were determined and the dissolved gases were analyzed; nonnitrated blanks were similarly treated and analyzed. In the experiments in which potassium nitrate was added, the nitrate was assumed to be completely reduced and an excess of dissolved nitrogen over that in the blank was found. The excess was practically equivalent to the nitrates reduced. This experiment when finished gave six sets of results, three of which were discarded on account of errors due to the difficulties of the analytical procedure. On the basis of the three remaining experiments the authors apparently assume that when nitrate is reduced it is converted quantitatively into nitrogen, for in subsequent experiments by these authors nitrate reduction is referred to as "loss of nitrogen." This, as will be shown later, is contrary to our experience.

[8] Chick, Harriette, "A study of the process of nitrification with reference to the purification of sewage," *Proc. Roy. Soc.* 78, 241-66 (1906).

[9] Muntz, A., and Laine, E., Études sur les eaux d'égout, *Ann. Inst. Nat. Agronomique,* 1907, VI, 15-143.

[10] Adeney, W. E., *App. VI to Fifth Report of Royal Commission on Sewage Disposal,* 1908, p. 13-20.

[11] *Opus cit.,* Table II.

K. Scheringa [12] claimed that with a concentration of 4 mg. of NH_4^+ and 2 mg. NO_2^- per liter the reaction $NH_4NO_2 \rightarrow N_2 + 2H_2O$ did not proceed. From the references cited we must conclude that there are no data in the literature showing that nitrogen gas is formed to any great extent during the reactions of sewage purification. The forms of nitrogen left undetermined by the earlier experimenters would probably have accounted for most of the "loss."

Recently, Buswell and Strickhouser [13] have presented the following explanation for the occurrence of nitrogen in the gases evolved during sludge digestion.

> The source of the nitrogen in the tank gases is not definitely known. Some claim that it arises from purely denitrifying reactions brought about by microörganisms. The writers have made a few simple calculations which show that the presence of large quantities of nitrogen in gases from new tanks may be explained on the basis of a reduced partial pressure in the digestion chamber. Since the dissolved nitrogen in fresh sewage or water used to fill the digestion chamber is in equilibrium with atmospheric nitrogen at a partial pressure of seventy-nine hundredths of the total atmospheric pressure, and the dissolved nitrogen in the tank sewage is in equilibrium with nitrogen at a partial pressure of say two-tenths of the total pressure of the gases in each bubble—i.e., 20 per cent nitrogen—it is clear that enough nitrogen must come out of solution to establish an equilibrium with the bubbles.
>
> As carbon dioxide and methane are formed in large quantities by microbiological action on the organic matter in the digestion chamber, such bubbles of gas are not in equilibrium with the dissolved gases. In accordance with Dalton's law of partial pressures, then, nitrogen will come out of solution until its concentration in the bubbles of gas is in equilibrium with the nitrogen concentration in the liquid.
>
> At 20° C. the solubility of pure nitrogen in water is 1.542 cc. per 100 cc. of water. In equilibrium with air, which is approximately 79 per cent nitrogen, the solubility is reduced to 1.219 cc. per 100 cc. of water. If the gas consists of 20 per cent nitrogen, then 100 cc. of water in equilibrium with the gas would contain 0.3084 cc. of nitrogen. If the percentage of nitrogen were reduced to 5 per cent, then, under the same conditions only 0.0771 cc. of nitrogen would be soluble in 100 cc. of water. Considering a gas containing 20 per cent nitrogen, each million gallons of sewage in the digestion chamber will produce 1220 cubic feet of nitrogen because of the decreased partial pressure effect alone.

[12] Rep. of Cent. Lab. Publ. Health, Netherlands, 1920, *U. S. Public Health Abstracts* 22.

[13] *Ind. & Eng. Chem.* 18, 407.

Theoretically, if this view is correct, the percentage of nitrogen in the gas should decrease as the digestion progresses and the soluble gaseous nitrogen has been liberated to a large extent in an effort to maintain equilibrium. This actual decrease has been found to occur. A calculation from the recent data of Bach and Sierp [14] on the nitrogen in gases from sludge digestion indicates that all of the nitrogen found by them may easily have been "swept out" of solution in the water in their reaction vessels instead of resulting from the decomposition of nitrogen compounds.

Nitrogen Fixation.

By purely chemical reactions nitrogen may be caused to combine in three well known ways: (1) Oxidation may be brought about by means of electrical discharge; which reaction occurs to a slight extent in nature during thunder storms; (2) reduction or combination of nitrogen with hydrogen can be brought about under proper conditions with the aid of catalysts, and (3) nitrogen may be combined with calcium and carbon, with the production of calcium cyanamide, $CaCN_2$. One can hardly imagine that these reactions could occur in nature. They have little more than theoretical importance in the present connection.

Nitrogen fixation is brought about in nature by means of the nitrogen fixing organisms, *Clostridium pasteurianum, Azotobacter,* and the symbiotic forms, all of which with other less known members of the group will be found described in any text on general bacteriology.

The course of the reaction by which these organisms effect the fixation of nitrogen is entirely unknown. To avoid complicating the diagram (Fig. 43) it is represented by a broken arrow passing through ammonia to protein. Since in general the reactions go on under anaërobic conditions there is some reason for the path chosen. Experimental results point to the fact that carbon compounds such as sugars are among the substances which stimulate these organisms, while soil biologists seem unanimous in the opinion that large amounts of nitrogenous organic matter, such as are found in sewage, would be unfavorable if not strictly inhibitory to these organisms.

It is pretty well known that most of the reactions shown in the figure take place in sewage purification. The occurrence of reactions 6, 4, 2, has only recently been demonstrated and there is some question whether nitrogen fixation takes place at all.

If the fixation of atmospheric nitrogen occurred during sewage

[14] *Centr. Bakt. Parasitenk. II Abt.* **58,** 401 and **59,** 1.

treatment it would be of tremendous economic importance. The evidence is worth considering.

Fowler,[15] in an extensive review of the conservation of nitrogen with special reference to activated sludge, states that "there is little doubt that not only does the activated sludge process recover the nitrogen present in the faecal matter of sewage but through fixation from the air an actual increase takes place over what can be recovered from the sewage." He bases this assertion on various experiments carried out by himself and co-workers. These experiments, which are described in some detail in the reference cited, we have summarized below.

(*1*) Experiments in which 50 cc. portions of activated sludge were aërated with and without the addition of 1 percent glucose showed 3.3 percent of combined nitrogen in the sludge to which no glucose had been added and 7.51 percent in the sludge to which glucose had been added. This experiment is interpreted by Fowler as indicating fixation of nitrogen. The result may, however, be due to the inhibition of denitrification by carbohydrates mentioned by Doryland.[16] No data is cited to show the total amount of combined nitrogen at the start and finish of the experiment.

(*2*) An experiment was carried out with activated sludge in a closed flask in which there was evidence of the absorption of gaseous nitrogen. The authors state, however, that the experiment should be repeated with an improved form of apparatus.

(*3*) In a small scale experiment with activated sludge, operated on the fill and draw plan, Fowler reports a 32.6 percent gain in nitrogen. He states, however, that "it should be mentioned that the Kjeldahl nitrogen was only determined in the initial and final sludge. Only the ammoniacal and the albuminoid nitrogen were determined in the sewage added and in the effluent. It is possible, therefore, that the value given for the gain in nitrogen may in consequence be somewhat too high, a greater proportion of Kjeldahl nitrogen being present in the sewage added than in the effluent passing away."

(*4*) In another experiment in which complete analyses of influent and effluent nitrogen were made, the apparent gain or fixation was only 4 percent.

(*5*) Experiments in which a substrate designed to favor nitrogen fixing organisms was inoculated with dried activated sludge and aërated, showed 15 percent to 25 percent fixation. On account of the small

[15] Fowler, C. J., "The nitrogen in activated sludge," *J. Indian Inst. Sci.* 3, 256-264.
[16] *Loc. cit.*

scale on which the experiments were carried out, the amount of nitrogen fixed was from 0.004 to 0.007 gm. The analytical methods are not given, and his evidence is far from conclusive.

The data given in Table 31 were collected with great care over a considerable period of time for the purpose of verifying, if possible, various claims of nitrogen fixation. The experiment was large enough (100,000 gallons per day) to give reliable results. The tabulation of the results is separated into ten to fifteen day periods, extending up to the end of the run.

The data are presented in this form in order to point out the danger of drawing conclusions from short periods of operation. For instance, it appears that from the 14th to the 21st of May, approximately 11 percent of the entering nitrogen was lost, while from the 2nd to the 15th of June there was an apparent gain of 25.7 percent.

Such a result as this last would lead one to infer that there must be considerable fixation of atmospheric nitrogen, while as a matter of fact, there was undoubtedly an accumulation of sludge from the preceding period which was drawn during the first two weeks of June. Averaging the results for the entire period we note the apparent gain of one and a half percent of nitrogen. When the difficulties involved in obtaining an average sample are considered as well as the limits of accuracy of the analytical procedure, we regard this value of one and a half percent as being within the limits of experimental error, and checking reasonably well with our loss of 0.4 percent, the result of the previous run. It has been claimed that in the presence of iron and crenothrix like organisms there was marked fixation of atmospheric nitrogen. From November 17 to December 27, ferrous sulfate was added to the screened sewage to the extent of 9.6 ppm. for ferrous ion for the purpose of stimulating these organisms. Table 31, however, indicates no fixation.

Recalling the broader meaning of "fixation," however, it should be noted that fixation of nitrate and ammonia nitrogen may take place by means of their syntheses into the insoluble microbial protein of the floc, occurring in the activated sludge process or the biological jelly of trickling filters.

Denitrification.

This process, the reduction of nitrates and nitrites, while brought about by bacteria, is not specific. A variety of organisms can effect the reaction, the presence of nitrates and easily oxidizable organic mat-

TABLE 31.—*The Nitrogen Balance.**

Duration of Run		Influent		Effluent		Sludge		Loss or gain of Nitrogen (Percent)
Date	Days	Average Gals/24 hrs.	Totals lbs. N_2 in Influent	Gals/24 hrs.	Total lbs. N_2 in Effluent	Total gals. drawn during run	Total lbs. N_2 in sludge	
May 3-13	11	88,200†	200.3	84,100	184.3	none	.....	— 7.9
" 14-21	8	86,700	163.9	85,600	122.2	9,050	23.68	— 10.9
" 22- 1	11	88,500	152.0	86,600	118.7	17,100	43.07	+ 6.4
June 2-15	14	91,400	273.0	85,200	176.1	87,150	166.85	+ 25.7
" 16-30	15	87,700	338.9	85,800	277.3	26,840	25.04	— 10.8
July 1-10	10	84,800	216.1	81,100	210.2	3,700	3.08	— 1.3
" 15-31	17	78,600	343.9	73,500	268.4	88,100	100.40	+ 7.2
Aug. 1-15	15	70,500	293.2	62,800	187.4	92,450	104.50	— 0.1
" 16-21	6	62,000	132.6	57,000	65.9	30,100	83.60	+ 12.7
" 22- 1	11	64,600	207.6	62,800	143.3	19,630	51.40	— 6.2
Sept. 2-20	19	66,500	345.3	64,900	248.4	4,460	129.20	+ 9.3
" 20-28	8	66,600	147.0	59,500	102.8	8,070	63.60	+ 13.2
" 29- 6	8	63,800	151.7	54,600	134.2	9,200	101.47	+ 55.3
Oct. 7-16	10	102,300	320.6	99,200	264.3	5,300	67.30	+ 3.4
" 17-31	15	93,800	486.2	89,100	374.1	4,900	117.20	+ 1.0
Nov. 16-30	15	80,500	273.1	80,500	240.7	none	.....	— 11.8
Dec. 1- 7	7	75,200	150.9	75,200	98.5	none	.....	— 34.7
" 8-28	21	77,800	508.6	75,300	316.8	3,800	172.18	— 3.8
Total	221	1,429,500	4,704.9	1,362,800	3,533.6	409,850	1,252.57	.....
Average		79,400		75,700	.....	27,300	.....	+ 1.8

* *Ill. State Water Survey Bull.* 18, p. 75.
† Includes filling the tanks.

ter being the only essentials. The products of the reaction include nitrogen, oxides of nitrogen, ammonia and protein. The production of the first three has been discussed above. The production of protein from nitrates as well as from ammonia has been noted by a large number of workers.[17]

It should be noted that the term denitrification in its strictest sense is used to indicate reduction of nitrates and nitrites with the loss of nitrogen. In a broader sense it may include the assimilation of nitrates mentioned above. Assimilation of nitrates and ammonia to form insoluble bacterial protein is sometimes referred to as nitrogen fixation, since the leaching out of nitrogen is thus prevented.

In the earlier experiments with the activated sludge process considerable attention was paid to the amount of nitrification, that is, the oxidation of organic nitrogen and ammonia to nitrates. Under such conditions protein synthesis could not, of course, be detected. Metcalf and Eddy,[18] quoting Hatton and Copeland's work,[19] report that in experiments at Milwaukee using as little as 0.67 cubic foot of air per gallon, clarification was obtained but no marked stabilization of the sewage. Reference to the table of data in the article cited above shows that using so small an amount of air there was a complete reduction of nitrites and a 50 percent reduction of nitrates. By using enough air so that decided nitrate formation was produced these workers obtained a clear and stable effluent. Their data do not, however, indicate the fate of the nitrates.

Our experience [20] with small amounts of air using sewage much higher in nitrates than the average, has shown that this nitrate oxygen may be utilized as a source of oxygen by the microörganisms in the sludge, while at the same time an effluent of reasonable stability is obtained.

Table 32 gives the amounts of nitrate and nitrite reduced during the successive periods of operation. As a matter of interest the oxygen has been recalculated in terms of cubic feet of oxygen and free air per 1,000,000 gallons. While this represents only a very minute fraction of the air used in maintaining the activated sludge process, it will

[17] Koch, A., and Pettit, H., "Uber den verschiedenen Verlauf der Denitrifikation im Boden und in Flussigkeiten," *Centr. Bakt. Parasitenk. II Abt.* **26**, 335; Doryland, C. J. T., *Expt. Sta. Bull.* 116 (1916); Voorhees and Lipman, *New Jersey Agric. Expt. Station, Bull. 221;* and others.

[18] *Amer. Sewerage Practice* **3**, 816.

[19] Hatton, T. Chalkley, "Activated sludge experiments at Milwaukee," *Eng. News* **75**, 306.

[20] Buswell, A. M., Brensky, A. A., and Neave, S. L., "Chemical and biological reactions in the Dorr-Peck tank," *Am. J. Pub. Health* **12**, 299 (1922).

TABLE 32.—*Reduction of Nitrates and Nitrites.**

Duration of Run			Nitrates and Nitrites				Nitrites				$NO_3 + NO_2$ (as N_2) reduced in lbs. per m.g.	Equivalent in oxygen supplied		Equiv. in free air cu. ft./ million gallons
Date		Days	Inf. ppm.	Eff. ppm.	Removal		Inf. ppm.	Eff. ppm.	Removal			lbs/ million gallons	cu. ft./ million gallons	
					ppm.	%			ppm.	%				
May	3-13	11	2.90	1.60	1.30	44.8	0.47	0.36	0.11	23.4	0.1560	0.5351†	5.9‡	28.1
"	14-21	8	2.10	0.22	1.88	89.5	0.32	0.05	0.27	84.3	0.2257	0.7741	8.7	41.4
"	22- 1	11	6.40	3.92	2.48	38.8	0.24	0.35	...	...	0.2977	1.0211	11.4	54.3
June	2-15	14	2.20	0.20	2.00	90.9	0.20	0.26	...	...	0.2401	0.8235	9.2	43.8
"	16-30	15	1.00	0.20	0.80	80.0	0.07	0.00	0.07	100.0	0.0960	0.3293	3.7	17.6
July	1-10	10	0.60	0.27	0.33	55.0	0.05	0.00	0.05	100.0	0.0396	0.1358	1.5	7.1
"	15-31	17	0.49	0.12	0.37	75.7	0.04	0.002	0.038	95.0	0.0444	0.1523	1.7	8.1
Aug.	1-15	15	0.80	0.20	0.60	75.0	.06	0.00	0.06	100.0	0.0720	0.2469	2.7	12.8
"	16-21	6	0.80	0.10	0.70	87.5	0.02	0.00	0.02	100.0	0.0840	0.2880	3.2	15.2
"	22- 1	11	0.70	0.10	0.60	87.5	0.04	0.00	0.04	100.0	0.0720	0.2469	2.7	12.8
Sept.	2-20	19	1.14	1.61	...	...	0.12	0.76	...	...	.....	.....	...	...
"	21-28	8	0.70	0.70	0.00	0.0	0.04	0.23	...	...	.....	.....	...	...
"	29- 6	8	0.60	0.60	0.00	0.0	0.05	0.02	0.03	60.0	.....	.....	...	...
Oct.	7-16	10	1.00	0.40	0.60	60.0	0.09	0.06	0.03	33.3	0.0720	0.2466	2.7	12.8
"	17-31	15	0.90	0.10	0.80	88.9	0.06	0.00	0.06	100.0	0.0960	0.3289	3.7	17.6
Nov.	16-30	15	6.50	7.00	...	...	0.79	0.90	...	...	.....	.....	...	...
Dec.	1- 7	7	3.50	1.70	1.80	51.4	0.53	0.19	0.34	64.1	0.2161	0.7403	8.3	39.5
"	8-28	21	4.50	2.00	2.50	55.6	0.43	0.13	0.30	69.8	0.3001	1.0282	11.5	54.7

* *Ill. State Water Survey Bull.* 18, p. 78.
† 14.01 parts of N_2 gives 48 parts of O_2.
‡ At 0° C., 760 mm., 1 cu. ft. O_2 = 40.482 gms. = 0.08936 lbs.

be seen that it represents a much larger portion of the air actually required for oxidation of sewage as calculated by Bartow,[21] namely, 0.05 cubic feet per gallon.

As may be seen from Figure 44, there is an appreciable decrease in both free and albuminoid ammonia in the effluent which is practically

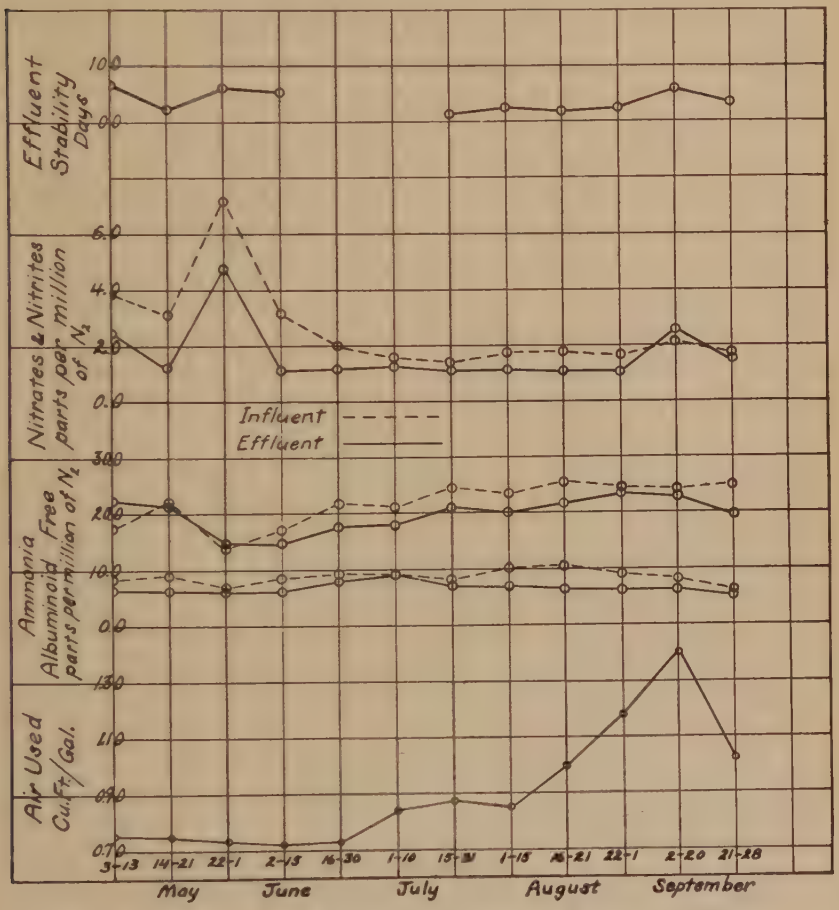


FIG. 44.—"Fixation" of Nitrates and Ammonia by Activated Sludge.

independent of the amount of air used. It is interesting to note, however, that when the air amounts to one and a half cubic feet per gallon the effluent and influent curves for nitrates cross—in other words, at this point nitrification takes place. Again, on reducing the air to one

[21] Crawford, F. N., and Bartow, E., "Composition of the effluent air from an activated sludge tank," *J. Ind. Eng. Chem.* 8, 646 (1916).

cubic foot per gallon there is a reduction of nitrates. These data lead to the conclusion that in the experiments reported in this paper the nitrification phase of the activated sludge process is entirely absent, and that nitrification is not essential to the success of the process. It is apparently possible under some conditions to produce clarification and reasonable stabilization of sewage operating with so little air that nitrate oxygen in the raw sewage is actually consumed by the microorganisms of the sludge. Attention should, however, be called to the fact that one maximum in the stability curve occurs simultaneously with the maximum influent nitrate and the other with the maximum air.

For the purpose of furnishing another example of the reduction of nitrates by sewage sludge, attention is called to the results of experiments carried on at the Lawrence Experiment Station (Mass. State Board of Health, Annual Reports 20, 115, 1920) for deodorizing septic sludge by means of nitrified effluent from trickling filters. In this experiment nitrified effluent was run into a tank containing septic sludge. The comparison of the analyses of the liquors added with those of the overflow from the tank shows that about 75 percent of the nitrate oxygen is used in stabilizing the sludge.

From the discussion of denitrification we see that there is abundant evidence that nitrates and ammonia are taken up by the organisms of the sludge and synthesized into protein rather than being lost as gaseous nitrogen. Protein formation must have occurred in our experiments, otherwise our nitrogen balance sheet would have shown a loss.

In an article by Richards and Sawyer [22] the conclusion is also reached that the biochemical reactions in this phase of the nitrogen cycle result in protein formation. Their summary is quoted.

> 1. If activated sludge is aërated for a short period in an ammoniacal solution the recovery of nitrogen is quantitative. The nitrogen not found as ammonia or nitrate in the effluent is recovered in the sludge.
> 2. If aëration is continued, loss of nitrogen occurs. The loss is roughly inversely proportional to the volume of sludge present.
> 3. The same effects are observed with sewage. The ammonia falls while the sludge gains nitrogen with a loss of nitrogen on the whole balance after sixteen days' operation.
> 4. There is considerable evidence that the extra nitrogen in activated sludge, over and above that found in the old type sludges, is derived from the ammonia of the sewage. There is no evidence of fixation of atmospheric nitrogen.

[22] *J. Soc. Chem. Ind.* 41, 62 T (1922).

The straw filter for sewage purification used by Richards and Weeks [23] takes advantage of this reaction. They state: "Laboratory experiments have shown that about 72 percent of the nitrogen content of sewage can be recovered by filtration through wheat straw at the rate of 250 gallons per cubic yard of straw per day. The best results were obtained after twenty days when the straw had become activated by bacteria present in the sewage. Operations on a larger scale showed a recovery of 65 percent of the nitrogen content of the sewage, the resulting manure being odorless and containing 2.06 percent of nitrogen."

Summary.

In summarizing the nitrogen cycle shown at the right in the diagram (Fig. 33) we note first that all of the changes are brought about by reversible chemical reactions which in practically all cases are catalyzed by bacteria. The usual course of mineralization is indicated by the arrows pointing straight downward from "protein" and under certain conditions, or when desired, the process may be interrupted at any one of the indicated steps. (For the sake of simplicity the intermediate steps in ammonification have been omitted.) The steps from ammonia to nitrate are peculiar in that they are brought about by specific organisms. At the nitrite stage the reverse action may be split into two paths, one of which gives nitrogen by reduction, and the other ammonia and protein by assimilation. The downward reactions result in the formation of nitrogen or its compounds which may ultimately be lost, while the upward reactions tend toward the retention of nitrogen as protein. If we classify the reactions under the two main headings, loss of nitrogen and formation of protein, they may be grouped as follows (the numbers refer to the corresponding numbers on Fig. 33):

Loss of nitrogen	as nitrogen	Reduction of NO_3^-	6, 7
		Oxidation of NH_3	9
		Auto-oxidation and reduction	7, 9
	as compounds of nitrogen	Soluble NH_4^+	11
		Soluble NO_2^-	14
		Soluble NO_3^-	15
		Volatile oxides	13
Formation of protein	by fixation	Bacterial	12
		Oxidation	2, 4, 8
		Reduction	2, 10
	by assimilation	NO_3^-	2, 4, 6
		NO_2^-	2, 4
		NH_3	2

[23] Richards, E. H., and Weeks, M. G., "Straw filters for sewage purification," *J. Soc. Chem. Ind.*, **40**, 252 R.

Chapter XVIII.

Sludge Digestion.

Outline of the Course of Sludge Digestion. The Digestion Spiral.

In nature organic matter is worked over and over by succeeding generations and classes of microörganisms until it has been broken down into simple substances, principally ammonia, nitrates and gases and a black residue vaguely referred to as humus. The course of this reaction might be represented by a spiral. Suppose at a point *A* (Fig. 45) we start out with the dissolved colloidal and solid organic matter in sewage. Microbial spores soon develop, producing bacteria, molds and higher forms whose nourishment is drawn from the organic matter. This assimilation goes on until eventually we arrive at point *B* where essentially all of the liquefied organic matter has been taken up to form the living substances of the growths which develop. If these growths continue their life processes they produce a certain amount of carbon dioxide, ammonia and other simple compounds and then eventually die and decompose, bringing us to the point *A'* where we again have dead and more or less liquefied organic matter. The distance from *A* to *A'* would represent what is referred to as the "wet-burning" or "moist combustion" which has taken place during the first lap around the spiral. In the meantime organic solids have been peptized or dispersed as the result of enzyme action, thus decreasing the apparent wet-burning in the liquid phase. The processes of growth, mineralization, death and liquefaction succeed one another as the rotting continues until only a resistant humus remains.

Sewage treatment by means of biolytic tanks, sprinkling or contact filters and subsequent secondary tanks gives us in a very broad way the results indicated by the spiral. The heavy solids are attacked and worked over by certain groups of bacteria in the sludge digestion chamber of the biolytic tank until practically nothing but a black humus remains. The liquefied products, together with the colloidal and dissolved organic matter in the sewage, are then taken in by the

organisms of the biological jelly on the sewage filter. In this jelly the same spiral of activities continues. A cross-section through the growth on the sewage filter stone shows on the outside the new whitish growth composed of various types of bacteria and protozoa. Just below this new growth there is a layer of less active and dying or dead bacterial filaments upon which varieties of protozoa are found feeding. The protozoa in turn die, and various forms, undoubtedly including some of the same anaërobic forms which are active in the sludge digestion chamber of the tanks, follow, producing immediately adjacent to the stone a black stable humus. This humus layer holds so much less firmly to the rock surface than the fresh growth that

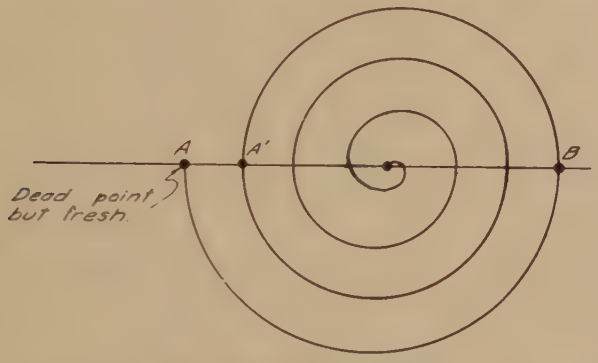


FIG. 45.—Digestion Spiral.

the mass breaks away in flocs and sloughs off from time to time, and is finally worked over in the digestion chamber of the secondary tanks. As a result of allowing this process to go on to the limit we obtain a relatively small amount of inoffensive humus-like sludge, a clear non-putrescible liquid effluent, and various gaseous products.

The digestion process mineralizes nitrogenous matter to such an extent that the digested sludge contains comparatively little nitrogen (about 2 percent) and has an almost negligible manurial value.

In the activated sludge process the aim is to carry the reaction only to point *B*. As soon as the dissolved and colloidal organic matter has been taken up by the growth of the floc forming organisms in the sludge the floc is separated from the clarified liquid and the portion in excess of what must be returned to the process is dried for fertilizer. This activated sludge is composed of fresh undigested organic matter, namely, the cells of the organisms developed in the process and, as would be expected, contains, when corrected for ash,

about the same amount of nitrogen as is ordinarily found in such cellular material. Without any ash correction activated sludge carries from 4 to 7 or 8 percent of nitrogen. It has been found to be of considerable value as a fertilizer.[1]

This conception of the reactions taking place during sewage purification is admittedly a highly idealized one and is used for the purpose of presenting a bird's-eye view of the whole question rather than to furnish a completed theory.

Chemical Reactions of Sewage Purification.

These chemical reactions which occur during the progressive change of fresh organic matter to oxidized or stabilized products may be of two kinds: (*1*) oxidation, resulting if complete in the formation of water and carbon dioxide and (*2*) formation of insoluble products. These insoluble compounds may be either solid or gaseous and may be the result of the following reactions:

(*a*) *Reduction,* resulting in the formation of methane and under some conditions hydrogen and the hydrocarbons of higher molecular weight.

(*b*) *Hydrolysis* or lytic actions in general, resulting in the formation of carbon dioxide and a variety of other products.

(*c*) *Humus formation.* Whether oxidation, reduction, or lysis appear to be the dominant reactions in the decomposition of organic matter, there is almost invariably a resistant, rather stable residue formed which is called "humus." This humus is of rather indefinite character and varies in composition depending upon the method and the material from which it is formed.

(*d*) *Bio-precipitation.* This process is best exemplified in the activated sludge process. It does not stabilize organic matter but removes it from dispersion in the sewage.

Stabilization of the Solids in Sewage.[2]

The solid organic matter which is deposited from sewage by sedimentation is usually associated with 90 to 95 percent of water from which it is not easily separated. It is soluble to a considerable extent

[1] Because of difficulties encountered in drying activated sludge some plants are adopting separate digestion of the sludge, temporarily at least. With this modification the reactions become like those in tanks and filters in their general course.

[2] There is so much active research in progress on this subject that the author regrets the necessity of preparing a summary at the present time.

although it goes into solution slowly and by means of rather complicated reactions. (*See* Chap. II.) The animal and vegetable matter of which it is composed consists largely of organic compounds containing either hydroxyl, carboxyl or amine groups or all three. These groups are soluble in water and act as solution links tending to favor the dispersion of the compounds in water. Many of these compounds are characteristically sticky or gluey, tending to take up water, first swelling to gels and then dispersing to sols. If solution, or perhaps more properly dispersion, of these solids is allowed to take place in such a manner that the liquefied products are returned to the main body of the sewage liquor the reduction in oxygen demand accomplished by sedimentation will be proportionately offset. The solids are of such a nature that they cannot be removed and exposed in the open air without creating a nuisance. They are allowed to undergo a rotting process while submerged and in a compartment or tank separated from the supernatant sewage liquors. The object of this rotting, as intimated in the discussion of the spiral, is to produce a relatively insoluble, inert, and stable organic residue of a compact granular texture which may be separated readily from the associated liquid by draining. This process is most often referred to as digestion but is sometimes called septicization.

Two Phases of Digestion.

From the standpoint of the resulting products this rotting appears to take place in two phases. Imhoff early designated them as the "putrid phase" and the "odorless phase." [3] In a discussion by Thumm and Reichle published in 1914 [4] the first phase was said to be of an acid character and the second phase of an alkaline character. Somewhat later Imhoff [5] uses the terms "acid digestion" and "methane digestion" to distinguish these two phases in the sludge rotting process. Groenewege [6] has also emphasized the occurrence of acid production during the early stages of putrefaction and a number of other workers

[3] Imhoff and Blunk, Ger. Pat. 275,498. May 1, 1912. U. S. Pat. 1,399,561. April 19, 1913; Imhoff, U. S. Pat. 1,399,562. Jan. 27, 1915; Imhoff, "Eight years of Imhoff tank design and operation," *Eng. News.* **75**, 14, (1916); Imhoff, "Separate sludge digestion and improved mixing in Imhoff tank." *Eng. Record* **74**, 101 (1916), also *Surveyor* **50**, 187 (1916).

[4] Feststellungen und Erfahrungen bei Emscherbrünnen, *Königl. Landesanstalt Wasserhygiene* **18**, 48.

[5] *Taschenbuch der Stadtentwässerung.* Oldenbourg, München. Third ed. 1922.

[6] "Bakteriologische Onderzoekingen over biologische Reinigung," *Mededeelingen van den Burgerlijken Geneeskundigen Dienst.* Deel 1. 1920.

have made similar observations. More recently Rudolfs [7] has studied the progress of putrefaction following the change in hydrogen-ion concentration as the process proceeds. His results confirm the observations of earlier workers, and with the aid of modern methods for the determination of hydrogen-ion concentrations he has been able to define the acid and alkaline phases of digestion more closely than was previously possible.

Acid Phase. When freshly settled sludge from domestic sewage is first drawn it has a pH in the neighborhood of 7. (By the "pH of a sludge" is meant the pH of the liquor associated with the sludge. The pH is determined on the liquid which is removed from the sludge by filtration, decantation or centrifuging.) If this sludge is allowed to stand at room temperature active biological action sets in within a few hours. There is an active evolution of gas, a considerable portion of the sludge is floated by the gas bubbles and the liquid portion becomes increasingly milky. At the same time the pH drops sometimes as low as 5 and an exceedingly foul odor develops, in which that of hydrogen sulfide appears to predominate.

The production of hydrogen sulfide is favored first by the anaërobic conditions which result in the reduction of sulfates to sulfides and second by the increase in hydrogen-ion concentration which displaces the following equilibria toward the evolution of hydrogen sulfide.

$$H^+ + HS^- \leftrightharpoons \underset{\text{in solution}}{H_2S} \rightleftarrows \underset{\text{gaseous}}{H_2S}.$$

During the "acid phase" there is relatively little decrease in the volume of sludge and little improvement in its drainability. In fact the early stages of acid digestion result in an increased stickiness. That the pH range, 5 to 6, is unfavorable for rapid peptization of nitrogenous compounds follows from the fact that the isoelectric points of those for which the data are known mostly lie a little below pH 5. This condition naturally retards the digestion of nitrogenous organic matter. Neave and Buswell [8] have shown a marked increase in the solubility of the organic matter in fresh sewage solids as the pH increases up to about 7.8.

The evolution of gas at this stage is relatively rapid. This rapid evolution of gas coupled with the sticky viscous character of the sludge presents ideal conditions for the formation of the foamy scum which is the frequent worry of operators of new plants. The gas

[7] *New Jersey Agr. Expt. Sta. Bull* **427.**
[8] *Ind. Eng. Chem.* **19,** 233.

which is formed during this acid stage phase contains a relatively large amount of carbon dioxide, frequeently 25 percent and sometimes as high as 50 percent. The quantity of methane is proportionately less, ranging from 50 to 65 or 70 percent. It is difficult to say, from the data at present available, to what extent the low methane content is due to the diluting effect of the carbon dioxide and to what extent it is due to less active methane fermentation than occurs in later stages. Some evidence favors the former explanation, namely, that methane is actively produced from the first but is diluted by the carbon dioxide until the evolution of carbon dioxide drops off.

In some cases, both in laboratory experiments and in actual plant operation, this acid condition predominates persistently and the digestion produces a foul sticky sludge which drains poorly. Numerous examples might be mentioned. We cite the experience of Stevenson,[9] in which a tank operated poorly and was persistently acid. The difficulty in this case was attributed to the high amount of fats in the sewage.

Alkaline Phase. Under proper conditions the acid phase of digestion is followed by an "alkaline phase,"[10] sometimes referred to as the "non-putrid" or "methane" digestion. During this stage the pH rises to between 7 and 8, the foaming usually ceases, there is a slight earthy or tarry odor, the amount of carbon dioxide in the gas drops and the amount of methane rises, the liquor loses most of its milkiness and the sludge becomes more granular.

This general improvement is due to the decomposition of the material which is more easily attacked by bacteria leaving a more stable, less soluble residue. Rudolfs,[11] for example, has shown that the biochemical oxygen demand of the sludge decreases rapidly as digestion proceeds. He found that in "ripe" sludge, i.e., sludge sufficiently digested to drain well and to undergo no further active fermentation during draining, the biochemical oxygen demand determined after 24 hours' incubation at 20° C. amounted to from 1000 to 1500 ppm. for each percent of organic matter. Or expressed as a formula for ripe sludge,

$$\frac{\text{biochemical oxygen demand in ppm. (24 hrs.)}}{\text{volatile organic matter in grams per 100 cc. sludge}} < 1500.$$

For fresh sludge the biochemical oxygen demand is several times as great.

[9] *Eng. News-Record* **75**, 430.
[10] Thumm and Reichle *loc. cit.*
[11] *Proc. 11th Annual Meeting New Jersey Sewage Works Assoc.* p. 24.

Neave and Buswell [12] have shown that during digestion a decrease in the "fixed carbon" of the organic matter occurs, similar to the change which takes place in coal in passing from lignite to anthracite. This change is not sufficiently great to permit the use of the fixed-carbon determination as a control test but it does indicate the trend of the reaction toward stabilization.

Methods of Maintaining Alkalinity. In a well-operating digestion chamber to which fresh solids are added continuously as in the Imhoff tank or at short intervals as in separate sludge digestion, the alkaline or non-putrid digestion should predominate. The acid condition should not recur after the first "working in" or "ripening" which occurs when the tank is first put in operation. Occasionally acidity has been observed in tanks from which nearly all of the digested sludge was drawn and on the other hand new tanks which were started off with an initial quantity of ripe sludge have been found to pass through the undesirable acid stage much more rapidly than those which were not thus treated. Thumm and Reichle [13] emphasized the importance of maintaining a proper ratio of "acid-binding" material to fresh sludge in any digestion chamber and securing a good mixture of the "acid-binder" with the incoming sludge. All of the present methods of maintaining an alkaline reaction ("acid-binding") during sludge digestion were given by these authors. These are:

(*1*) By maintaining the alkalinity of the fresh sewage liquor which may be caused to enter the digestion chamber.

(*2*) By introducing tap water which will both neutralize and dilute the acid.

(*3*) By introducing nitrogenous matter which during digestion forms ammonia (i.e., sludge which has passed the acid stage).

(*4*) By the addition of alkali (lime, limestone, etc.) in the chambers.

The necessity of having a considerable excess of ripe sludge over fresh solids to maintain alkaline or non-putrid digestion in the chamber was thus early recognized. Imhoff [14] suggested a special device to mix a predetermined amount of ripe sludge with the fresh solids, basing his patent on the above observations. The amount of ripe sludge necessary to maintain proper digestion he states [15] will vary with local conditions but suggests the retention of ripe sludge equal to one month's accumulation or 1 part of fresh solids to 30 parts of ripe sludge.

[12] *Loc. cit.*
[13] *Loc. cit.*
[14] U. S. Pat. 1,399,561 (1913).
[15] *Eng. News-Record* **75**, 52.

For a separate digestion system at Birmingham, Watson [16] uses 1 part ripe sludge to 5 parts of fresh sludge with most excellent results. Artificial heating is used at times in this plant. Rudolfs [17] has recently determined the ratio of fresh solids to sludge for Plainfield, New Jersey, and finds it to be 1 to 50 at ordinary temperatures.

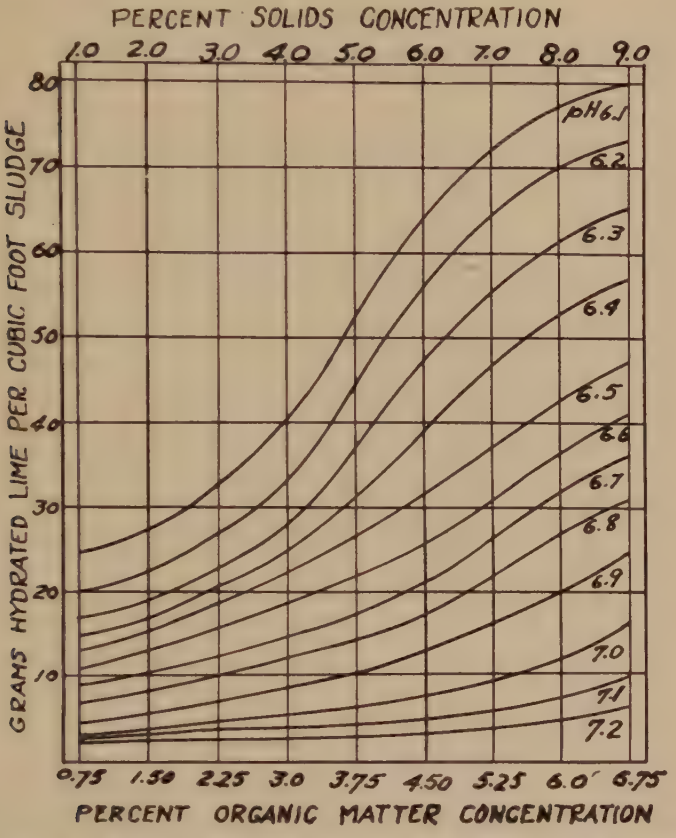


FIG. 46.—Lime Required for pH Adjustment of Sludge (after Rudolfs).

Optimum pH for Digestion. Rudolfs has further observed that the best digestion occurs at Plainfield when the pH lies between 7.3 and 7.6. About the same range for good digestion was noted by Baity.[18] An increase of the ratio of fresh solids to sludge lowers the pH and results in poorer digestion. This is in accord with earlier observations

[16] *Eng. Contr.* 52, 85 (1924).
[17] *Loc. cit.*
[18] *Ibid.*, p. 29.

of Imhoff and others. If lime is added to maintain the proper pH this ratio may be increased to 1 to 20, thus greatly increasing the capacity of the tank. The detailed directions for the addition of lime are given by Rudolfs as follows:

> If we wish to change the pH value of a given material of any concentration to any other pH value by adding the amount of lime needed, there are three variables. Curves constructed with three variables are more or less complicated, and since we have found that optimum digestion takes place at pH values of 7.3 to 7.6, we have constructed a set of curves (Fig. 46) which shows at a glance the number of grams of hydrated lime to be added per cubic foot of fresh solids or partly decomposed material to adjust the material to a pH value of 7.3. Ordinarily the amount of solids received at a plant is known. The organic matter content varies only slightly at a given point. At Plainfield the variations during a year (analyses every two or three days) were not more than 2 or 3 percent in the settled solids. The total amounts of hydrated lime needed for the Plainfield plant (220 ppm. settleable solids with about 75 percent volatile matter) are about 3 or 4 pounds per million gallons of sewage daily to adjust the material in the digestion chamber to a pH value of 7.3. This is the amount needed after the contents in the digestion chamber have reached this figure. If sufficient sludge capacity is present even less or nothing at all is required.
>
> But what must be done to correct a poor working, acid-foaming tank? Let us take some examples:
>
> 1. A tank is foaming but there are still distinct sludge, liquid and scum layers.
>
> First we must find approximately how much sludge and scum is present and ascertain their solid concentrations.

Capacity of digestion chamber	10,000 cu. ft.
Sludge (8% solids)	3,000 cu. ft.
Scum (6% solids)	1,000 cu. ft.
Liquid (0.5% solids)	6,000 cu. ft.
Average solids for chamber	3.3%
pH value of liquid	6.8

> When distinct layers are present it will be found that the percentage solids in the liquid is very small, perhaps 0.1 to 0.2 percent, and the liquid layer can then safely be disregarded. Now let us turn to the curve. With a solids concentration of 3.3 percent and a pH value of 6.8 the amount of lime required per cubic foot material is 10.7 grams or a total amount of lime for the whole tank of 220 pounds to change the reaction to 7.3.
>
> 2. An aggravated case of foaming.
>
> There is no definite scum or sludge layer but the solids are distributed throughout the tank. All that is necessary is to determine the solids from a sample taken sufficiently deep to insure approximately average conditions, and pH values determined. Then use

the chart for the amount of lime necessary per cubic foot. A simple calculation tells the amount of lime needed for the whole tank.

If more accurate determinations are desired or can be made, it is better to calculate the amount of lime needed on the basis of volatile matter, because the ash content of different sewages is not alike, especially where industrial wastes are received.

It should be borne in mind that frequent small additions of lime to Imhoff tanks (when required) are far better and more economical than additions of lime at long intervals. In other words, it is easier and cheaper to prevent an aggravated form of foaming than to cure one.

In separate sludge digestion tanks, fresh solids should be added every day. The fresher the solids the more easily they are controlled and the more economical it will be. These fresh solids should be adjusted every time they are added rather than to make an effort to adjust the whole tank when a large amount of fresh solids is accumulated. Separate sludge digestion tanks seeded with sufficient ripe sludge will remain almost indefinitely at the proper pH value provided the relation of fresh solids and ripe sludge is kept correct and the fresh solids are really fresh (added every day as soon as they are settled). None or very little adjustment of the fresh solids will be necessary unless acid industrial waste is present.

If the relation of fresh solids to ripe sludge is correct in Imhoff tanks and the incoming sewage averages about pH 7.5-7.6, lime will not be necessary unless sudden changes occur like additions of acid trade waste, mash from illicit distilleries, etc. The reason why mash is mentioned in particular is because this material produces large quantities of organic acids in the course of its decomposition. If the average pH values of incoming material are lower, a constant careful control will prevent a good deal of nuisance and expenditure of money.

Occasionally when a tank is adjusted the fluctuations in the reaction of the material are great and sudden with the subsequent result that biological activities will undergo greater and more rapid changes and in some cases, where the tank was very acid, a possible apparent retardation of digestion seems to take place. It is possible that under certain conditions (comparatively high temperatures or absence of appreciable quantities of ripe sludge, for instance), digestion activities will become so rapid that it at first appears as an aggravation of the troubles. These more violent manifestations of activities, whether desired or not, might at first dishearten the operator but the ultimate result will be beneficial although conditions ad interim may not be all that is desired.

For the correction of an Imhoff tank we have found that additions of dry hydrated lime to the digestion compartment with the aid of a small pump for mixing it with the liquid, sludge and scum gave good results. The material was pumped out of one compartment into the other and the lime added to the material at the end

of the hose with a dry feed mixer. This insured fairly good mixing but this method can easily be improved upon. In some plants perforated pipes are available and milk of lime could be used instead of dry lime. Dumping large quantities of lime into one digestion chamber is not advisable, since the lime will sink to the bottom and cause locally strong caustic concentration with consequent partial sterilization.

For the adjustment of a separate sludge tank a similar procedure can be followed, while adjustment of settled solids which are pumped to the tank can be adjusted at the time of pumping. Sprinkling of lime on top of the scum at frequent intervals is also possible but the reaction on the whole tank, particularly the partly decomposed material lying on top of the sludge, will not receive such rapid benefit and conditions will not be corrected as rapidly and thoroughly.

There are cases where the addition of lime is not found as beneficial as it was by Stevenson (cited above) and Rudolfs. Imhoff [19] reports that in Germany liming of digestion chambers has been tried repeatedly but never with success.

The optimum pH range of 7.3 to 7.6 determined by Rudolfs is apparently not of universal application. Dr. W. D. Hatfield [20] states that at Decatur, Illinois, where an exceptionally well-digested sludge is obtained the pH is in the neighborhood of 6.8. At this plant the temperature of the incoming sewage is near 35° C. due to industrial wastes.

Three explanations may be given for the maintenance of a relatively high pH in the digestion chamber in the presence of an excess of ripe sludge. The microbial population of the ripe sludge may overgrow and choke out the acid producers which apparently thrive on the fresh material alone, or what seems more probable, the alkaline products produced by the decomposition which occurs in the second phase are more than sufficient to neutralize the acids produced in the first. In other words, the ripe sludge acts as an alkaline buffer maintaining a relatively constant pH. It is also known that the acids may be decomposed by bacterial action instead of neutralized.

Sources of Acidity. From the discussion in the previous chapter it is apparent that the acid produced in the first stages of digestion may arise (*1*) from the decomposition of carbohydrates, (*2*) from the hydrolysis and oxidation of fats and (*3*) from the hydrolysis and deamination of proteins. Experimenters seem quite well agreed that very little protein decomposition occurs during the first stage. That

[19] *Eng. News-Record* **75,** 52.
[20] Private communication.

leaves carbohydrates and fats as the source of the acid. The simpler carbohydrates (e.g., the sugars and starches) are easily and rapidly decomposed but the usual chemical tests fail to reveal more than very small quantities of these substances in fresh sewage sludge. The more complex carbohydrates, such as natural cellulose, are only very slowly attacked their decomposition requiring months. That the amount of acid observed in the first stage of sludge digestion comes largely from the carbohydrates seems improbable. Numerous references in the literature indicate that grease is broken down during sludge digestion.

O'Shaughnessy,[21] for example, stated that the fats and soaps are about 30 percent decomposed and recently Neave and Buswell[22] have made a similar observation. The latter authors found the same percent of "grease" in fresh solids and digested sludge, indicating that the digestion of this material kept pace with that of other organic matter. (See also Bach and Sierp.[23]) Later work by the same authors (as yet unpublished) indicates that the "grease" or "fats" are largely decomposed during the first phase of digestion to give acetic, butyric and others of the lower fatty acids.

Source of Alkalinity. The alkaline reaction of the second phase of digestion is generally considered to be due principally to the ammonia produced by the decomposition of nitrogenous matter. The decarboxylation of fatty acids also tends to reduce the acidity thus:

$$CH_3 . COOH \rightarrow CH_4 + CO_2.$$

Two-Stage Digestion. In a number of separate sludge digestion installations abroad the practice is to carry on the digestion in two stages. The fresh sludge is allowed to remain in the first digestion tank for about half the total time required for digestion and then removed to a second tank for the completion of the process. This procedure precludes any possibility of the presence of undigested particles in the sludge when drawn off to the drying beds. An exceptionally good sludge is obtained at Birmingham, England, in this way. The Kremer design of tank used in Germany operates on this plan.

The Residue from Digestion. Humus.

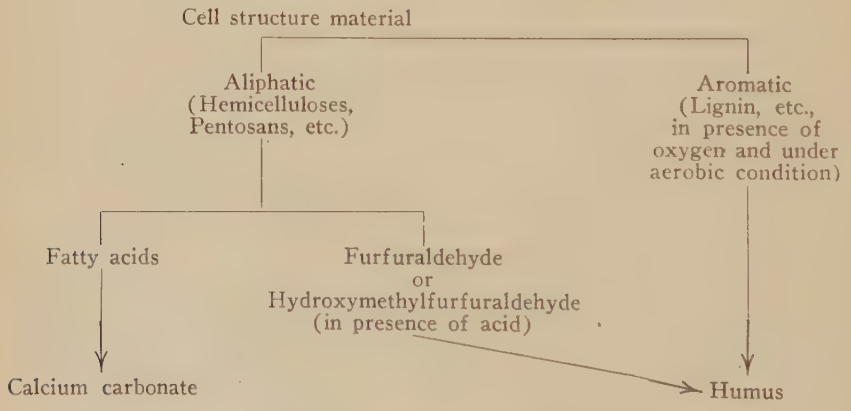
The net effect of all of these biochemical reactions is to break down some of the less complex compounds to the gaseous end-products carbon dioxide and methane and at the same time to remove the solu-

[21] *J. Soc. Chem. Ind.* **33**, 3R (1914).
[22] *Ind. Eng. Chem.* **19**, 234.
[23] *Centr. Bakt. Parasitenk.* II Abt. **60**, 318 (1923).

tion link groups from the more complex compounds, thus leaving a relatively inert solid residue which has a greatly decreased affinity for water. Spillner,[24] describing an early and extensive series of experiments on the drying qualities of both fresh and digested sludge, gives considerable data illustrative of this change. Fresh sludge when drained to a gel of spadable consistency retained 71 percent moisture while spadable digested sludge retained only 55 percent moisture. The fresh sludge required 33 days to drain, the digested sludge 16. Digested sludge usually contains 80 to 85 percent moisture when drawn from the tanks and occasionally runs as low as 70 percent, while fresh sludge seldom carries as little as 90 percent moisture. These figures indicate clearly the presence of water-binding colloids in fresh sludge.

The degree to which the colloids have been digested may be judged from the size and number of the cracks which appear when the sludge is dried on the drying bed. Well-digested granular material will show a large number of small cracks an inch or more apart, while poorly digested sludge will show wide cracks several inches apart.

The stable residue is commonly referred to as "humus." The term "humus" is one of rather indefinite significance and may be used to designate the resistant material which remains after the decomposition of organic matter by various chemical reagents or by microörganisms. The chemical composition of humus depends upon the character of the material from which it is formed as well as upon the method of its formation. The following schematic representation of the humus formation is suggested by Russell:[25]



[24] Elsner, Spillner and Allen, *Sewage Sludge*, McGraw-Hill, 1912.
[25] *Microörganic Population of the Soil*, p. 169.

The amount of this humus residue varies considerably with the character of the raw sludge. O'Shaughnessy [25] reported that the amount of sludge decreased to the extent of 30 percent in about seven weeks but the product was sticky. A further period of several weeks was required for a physical change in the sludge as a result of which it became granular. A digestion period of several years still left 40 percent of the organic matter undissolved. Early investigators claimed a much higher degree of liquefaction. In modern practice about 25 to 35 percent of the organic matter is liquefied and gasified during digestion. The *volume* of the sludge is reduced in a much greater ratio than is the weight, due to the destruction of the water-binding colloidal character of the organic matter. The volume reduction may frequently amount to 75 percent.

Effect of Temperature on Digestion.

The effect of increase in temperature during digestion is to greatly increase the rate of organic decomposition. The optimum temperature for rapid stabilization of solids appears to be about 37° C.[26] Whether or not the temperature changes the course of the reaction has not yet been established. The increase in rate of gas production goes along with increased decomposition of solids but appears to reach a maximum at a temperature 5° to 10° C. lower. Rudolfs [27] states that the total gas per gram of organic matter is not increased by increase in temperature.

Since with an increased temperature the rate of digestion is increased, a smaller tank capacity may be used to handle a given amount of sludge if artificial heating is provided. The advantages of such an arrangement have not so far been generally considered worth the extra operation expense. There are some cases in which the cost of heat is distinctly less than the interest on the extra cost of larger tanks. The quantitative relation between temperature and rate of digestion is difficult to define because of rather wide differences in the methods of measuring digestive progress. Sierp [28] has shown that the evolution of gas is best at 25° C. but that liquefaction is most rapid at 37°. He does not recommend heating above 25° in practice. He found that gas production was arrested at 6° but that there was still

[25] *Loc. cit.*
[26] Bach and Sierp, *loc. cit.*
[27] *Loc. cit.*
[28] *Technisches Gemeindeblatt* **27**, 213, 229.

some decomposition at that temperature. More recently Baity [29] has furnished similar data:

> The total time required for the digestion of this sludge at 10° C. is estimated at more than a year; the time required at 20° C. is about 130 days; at 25° C. one hundred days are necessary; and at 38° C. about 85 days are required. This is for complete digestion. A better idea of the probable time required at different temperatures for digesting this sludge (under natural conditions), sufficiently to draw onto drying beds is given by the periods between the beginning of the experiment and the peaks of gas production. At 10° C. this is estimated at more than nine months; at 20° C. it was 70 days; at 25° C., about 54 days; and at 38° C. about 58 days were required. With reference to gas production, it is notable that at all temperatures the total amount of gas produced during digestion was the same. The rates of production were different, as were the periods required for digestion, but the ultimate quantities of gas evolved were practically identical.

Bach and Sierp [30] have reported the degree to which various ordinary foods and feces are liquefied by sewage bacteria as shown in Table 33.

TABLE 33.—*Summary of Digestion Data.**

Material	Liquefaction and digestion
	Percent
Raw meat	91.3
Cooked meat	90.6
Indigestible meat residues	80.
Cooked egg white	96.7
Dextrose	100.
Fresh carrots	83.3
Dried carrots	75.2
Raw potatoes	57.2
Cooked potatoes	83.
Washed feces	49.

* Bach and Sierp, *Centr. Bakt. Parasitenk.* II Abt. **60,** 318 (1923).

Gas Formation.

The earliest investigators appear to have realized that the gases given off during putrefactive fermentation contained considerable amounts of methane, and various arrangements were made from time to time to use the methane as a source of heat or power. Cameron used the gases from his plant at Exeter, England, for lighting more than twenty-five years ago. Gas from sewage tanks was used at Matunga, Bombay, for driving a gas engine in 1897,[31] by Hommon [32]

[29] *Loc. cit.*
[30] *Loc. cit.*
[31] *Eng. News* **58,** 146.
[32] *Eng. Record* **73,** 182 (1916).

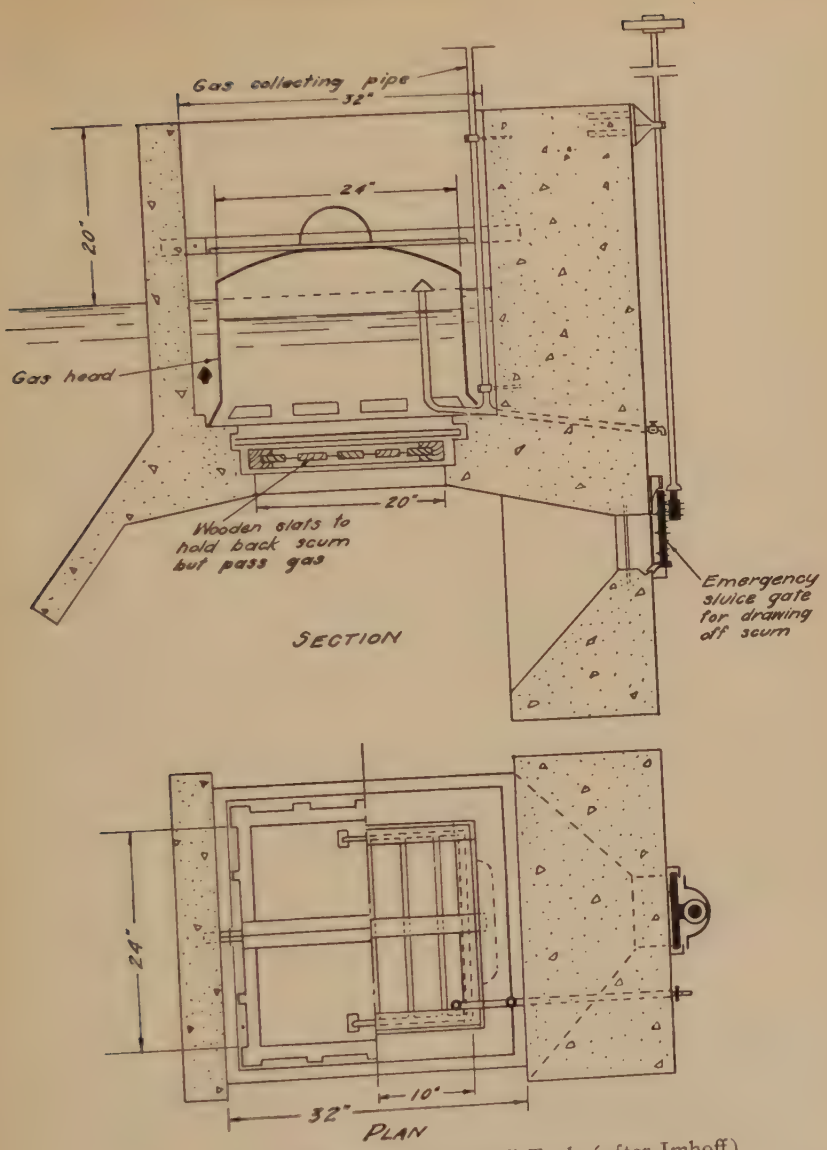


FIG. 47.—Gas Collector for Imhoff Tank (after Imhoff).

for lighting in 1915 and by Watson [33] in Birmingham in 1920 for power production. Moss-Fowler [34] in 1923 reported the work of Flicker begun in 1911 in Australia on the production and collection

[33] *Eng. News-Record* 87, 1062.
[34] *Surveyor* 63, 181.

of gases from sewage tanks. Several of the devices for stimulating gas production and collection have been patented.

Recently Imhoff [35] has described certain installations in Germany completed in 1922 for the collection and use of the gas. When applied to two-story tanks the gas collectors replace the former gas vents, the gas rising to a collecting bell (*see* Fig. 47) which is water sealed. The floating particles of sludge are prevented from entering the bell by a grid or grill. As soon as the gas has worked its way out of the sludge particles they sink instead of drying out and forming a scum as they do in the gas vents of an ordinary tank. Provision is usually made for the removal of any persistent scum but experience has not shown it to be necessary. Incidentally the substitution of gas collectors for gas vents increases the area of the sedimentation chamber about 25 percent.

The amount of gas obtained from sludge digestion is naturally variable. Imhoff obtains about a third of a cubic foot per capita per day of a gas which contains 80 to 85 percent methane from settled sludge. Flicker reported three cubic feet per capita per day of gas with a B.t.u. value of 600 per cubic foot, the Bombay installation yielded three to four cubic feet of gas per capita per day, Watson obtains one cubic foot of gas from 0.36 pound of sludge (dry weight) and Hatfield [36] reports from two to four cubic feet per capita per day at Decatur, Illinois, where there is a large amount of warm wastes from a starch factory.

As mentioned above, sewage tank gases usually contain from 65 to 80 percent of methane, occasionally a small amount of hydrogen and the remainder is carbon dioxide and nitrogen together with a detectable amount of hydrogen sulfide in most cases. Tables 34 and 35 show some of the variations in composition which have been observed.

TABLE 34.—*Volume of Methane in Septic Sewage Gas.**

	Percent
Exeter (Donald Cameron)	20.13
Exeter (Donald Cameron)	24.4
Matunga (C. C. James)	21.25
Matunga (C. C. James)	23.9
Lawrence (Mass. State Board of Health):	
Septic Tank A	79.0
Septic Tank B	37.5
Septic Tank F	75.9
Parramatta (Septic Gas Co., of Australia)	60.0
Birmingham (J. D. Watson), Aug. 1921	60.1
Sept. 1921	77.0
Nov. 1921	67.5

* Watson, *Eng. News-Record* **87**, 1062.

[35] *Fortschritte der Abwasserereinigung*, 1926.

[36] Private communication.

TABLE 36.—*Sewage Tank Gas Analyses.**

Date	Source	Location	CO_2 *per-cent*	H_2S *per-cent*	O_2 *per-cent*	H_2 *per-cent*	CH_4 *per-cent*	N_2 *per-cent*	Remarks
		From Foaming Tanks							
Sept. 2, 1924	Decatur	Tank 3, middle vent	29.4	0.1	0.0	0.0	66.6	3.9	
" 9, 1924	Decatur	Tank 1, middle vent	29.3	..	0.0	0.0	67.5	3.2	
" 9, 1924	Decatur	Tank 1, middle vent	28.5	..	0.0	0.0	65.7	5.8	
" 26, 1924	Decatur	Tank 1, middle vent	28.3	..	0.0	0.0	67.7	4.0	Foaming only slightly
Oct. 4, 1924	Highland Park	East tank, effluent end	24.0	..	0.0	0.0	72.7	3.3	Park Ave. plant
" 4, 1924	Highland Park	East tank, influent end	24.7	..	0.0	0.0	71.3	4.0	Park Ave. plant
July 14, 1925	Urbana	North tank, middle vent	22.6	..	0.6	0.0	62.5	14.3	Beginning to foam
Oct. 13, 1925	Urbana	Tank 3 resting, middle vent	19.8	0.0	0.3	0.0	68.7	11.2	
" 15, 1925	Urbana	Tank 3 resting, middle vent	20.1	0.0	0.3	0.0	68.0	11.6	
	AVERAGE		25.2	...	0.1	0.0	67.8	6.8	
		From Nonfoaming Tanks							
Sept. 2, 1924	Decatur	Tank 1, side vent	25.9	0.1	0.0	0.0	71.4	2.6	
" 9, 1924	Decatur	Tank 3, middle vent	28.5	..	0.0	0.0	63.0	8.5	
" 26, 1924	Decatur	Tank 1, middle vent	23.6	..	0.0	0.0	72.8	3.6	
Oct. 4, 1924	Highland Park	Side vent	3.3	..	0.0	0.0	78.2	18.5	Deerfield plant
May 1, 1925	Urbana	North tank, middle vent	16.2	..	0.6	0.0	60.0	23.2	
" 7, 1925	Urbana	North tank, middle vent	11.6	..	0.0	0.0	67.2	21.2	
" 19, 1925	Urbana	South tank, middle vent	10.0	..	0.2	0.0	70.7	19.1	
July 28, 1925	Urbana	South tank, middle vent	15.3	..	0.3	0.0	68.6	15.8	
	AVERAGE		16.8		0.1	0.0	69.0	14.1	
		From Septic Tank							
Aug. 22, 1924	Urbana	East tank	14.0	..	0.0	4.5	66.4	15.1	
" 26, 1924	Urbana	East tank	14.3	0.5	0.0	5.0	64.3	15.9	
" 29, 1924	Urbana	East tank	13.6	..	0.0	3.5	72.5	10.4	
July 14, 1925	Urbana	East tank	17.0	..	0.0	0.0	78.0	5.0	
	AVERAGE		14.7		0.0	3.3[a]	70.3	11.6	

* Buswell & Strickhouser, *Ind. & Eng. Chem.* **18**, 407 (1926). [a] Includes analysis of July 14, 1925, when no hydrogen was found.

TABLE 35.—*Analysis of Birmingham Septic Tank Gas, September and November, 1921.*[1]

	Percent	Percent
Carbon dioxide CO_2	18.1	25.2
Hydrocarbon HC	0.2	....
Oxygen O_2	0.4	0.3
Carbon monoxide CO	1.1	....
Methane CH_4	77.0	67.5
Ethane C_2H_6	trace	2.8
Nitrogen N_2	3.2	4.2
	100.0	100.0
B.t.u. per cubic foot	700	650

[1] Watson, *loc. cit.*

Source of Methane. Leaving out of consideration for the moment the earlier steps in the decomposition which result in methane production, we find that acetic acid or rather its salts such as calcium acetate seem to be its immediate source. Groenewege [37] points out that the bacterial decomposition of calcium acetate with the formation of methane was first discovered by Hoppe-Seyler [38] and that in 1906 Söhngen [39] developed a decantation method, similar to the fill-and-draw activated sludge process, for producing a sludge rich in methane fermenters which would catalyze the reaction

$$Ca(CH_3CO_2)_2 + 2H_2O \rightarrow Ca(HCO_3)_2 + 2CH_4.$$

Groenewege further reports "that methane can arise not only from calcium acetate but also from calcium formate, calcium butyrate, salts of higher fatty acids with an even number of carbon atoms, acetone, methyl, ethyl and *n*-butyl alcohols, glucose, lactose, peptone, egg albumin, pectin ("Holzleim") and gelatin." Bach and Sierp [40] have repeated the work of Söhngen using digested sludge and find that calcium acetate may be rapidly decomposed by this means, giving methane and carbon dioxide. Repeated decantation produced a more active sludge.

Various statements in the literature have led to the belief that the methane in sewage tank gases was produced by the decomposition of carbohydrates. But since all of the simpler substances (fatty acids, etc.) from which it is formed are known to result from the decomposition of fats and proteins as well, there seems to be no reason for such a limitation. Methane *may* arise from the decomposition of

[37] *Loc. cit.*
[38] *Z. physiol. Chem.* Bd. II, 561 (1887).
[39] *Proefschrift,* Delft, 1906.
[40] *Loc. cit.*

simpler carbohydrates as was shown in a previous chapter, but it may also be formed by the decomposition of fats and proteins. Since the amount of carbohydrate decomposition is relatively small under ordinary conditions, it is apparent that the fats and proteins must be looked to for the source of methane.

Some light is thrown on the probable source of methane by the data quoted from Ruge by Mathews [41] on the composition of gases resulting from intestinal putrefaction in subjects on various diets:

	Carbon dioxide *percent*	Hydrogen *percent*	Methane *percent*	Nitrogen *percent*
Vegetable diet	21-34	1.5-4	44-55	10-19
Meat diet	8-13	0.7-3	26-37	45-64
Milk diet	9-16	43-54	0.9	36-38

A more specific investigation has been made by Bach and Sierp [42] who studied the course of decomposition of various typical food substances. They summarized their results as shown in Table 37.

Source of Hydrogen. The formation of occasional small amounts of hydrogen is explained by Groenewege as follows:

> Hydrogen arises exclusively in anaërobic processes; its sources are:
>
> *1.* Pectose digestion—the "middle lamella," consisting of pectin substances, which occurs between the cell walls of parenchymous tissue, is dissolved under the influence of butyric acid ferments; in this process there arises mainly carbon dioxide, hydrogen and volatile fatty acids (mainly acetic and butyric).
>
> *2.* The digestion of different carbohydrates, among others glycerin, mannite, dextrin and starch, by butyric acid ferments giving also acetic and butyric acids. Frequently only small amounts of acid arise, the main product being alcohols, particularly butyl alcohol.
>
> *3.* The digestion of salts of formic acid giving hydrogen and carbon dioxide by means of the *Bact. formicicum* of Omeliansky.
>
> *4.* The digestion of proteins.
>
> In digestion experiments seeded with sludge, using any of these materials, much less hydrogen is evolved than is to be expected. This is apparently due to the union of the hydrogen with carbon dioxide, thus:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O.$$

The fact that little or no hydrogen is present in the gas as collected is attributed by Söhngen, Groenewege, and Bach and Sierp to

[41] *Textbook of Physiological Chemistry*, p. 440.
[42] *Loc. cit.*

the observation that sewage sludge catalyzes the latter reaction and Imhoff and Hilgenstack have patented a process making use of this.[43]

Disposal of Sludge.

The ripe granular sludge resulting from thorough digestion is ordinarily pumped or siphoned from the bottom of the digestion chamber

TABLE 37.—*Gases Formed during the Anaërobic Digestion of Certain Organic Substances.**

Substance used	Total gas evolved, cc. per gm. substance	Total gas evolved, cc. per gm. dry solids	Character of gas
Raw meat	14	54.5	Chiefly CO_2; CH_4 low, never over 33%; H_2 present at start only.
Cooked meat	12 (not corrected for gas in solution)	46.6	Similar to raw meat, but CH_4 slightly higher.
Indigestible meat residue	12.9	50	CO_2 and CH_4 high; H_2 only in traces.
Cooked egg albumin	40 (not corrected for gas in solution)		CH_4 very high; CO_2 never over 25%.
Dextrose	17 (not corrected for gas in solution)	17	H_2 and CO_2 high; CH_4 only in traces.
Fresh carrots	64	526	CH_4 increasing up to 42%; rest chiefly CO_2 except at start when H_2 was almost 50%.
Carrots dried at 100° C.	528	528	At first high H_2 and CO_2 later H_2 absent and increasing CH_4.
Raw potatoes	40	247	Chiefly CO_2; H_2 up to 25%; CH_4 only in traces.
Cooked potatoes	100	410	CO_2 and H_2; traces of CH_4 near end of digestion.
Washed feces	142	739	CH_4 high; decreasing CO_2; H_2 only at start in small amounts.

* Bach and Sierp, "Untersuchungen über den anaeroben Abbau organischer Stoffe durch Bakterien des Klärschlammes," *Centr. Bakt. Parasitenk., Abt. 2*, **62**, 24-76 (1924).

on to sand beds (*see* p. 220). The sand beds are usually provided with underdrains and are bounded by low walls extending a foot or two above the sand. In some cases[44] glass-covered beds have been used to hasten drying and avoid odors. The sludge though carrying as low as 70 percent moisture in some cases is sufficiently fluid so that

[43] Ger. Pat. 411,926. Feb. 10, 1922.
[44] *Nation's Health* **8**, 128.

it may be pumped and distributed to the various sand beds by means of troughs. In ordinary weather the sludge will drain and evaporate sufficient moisture in two to three weeks so that it may be easily handled with a shovel (spadable). It is then shoveled into carts or narrow-gage cars and hauled away to be used for fill or fertilizer. The value of the sludge for fertilizer depends upon its humus character rather than on its content of plant foods such as nitrogen and phosphorus. The nitrogen content ranges from 1 to 2 percent on the dry basis and the phosphorus about the same. At Rochester, New York, for example, a small price is received for the air-dried sludge.[45]

The air-dried sludge was further dried by heat at Baltimore for a number of years [46] and sold as a fertilizer base. The process resulted in a loss of about 50 cents per ton. The air-dried sludge is now given to farmers who are willing to haul it away. If the nitrogen content had been 4 percent instead of about 2 percent heat drying would have been successful.

A fertilizer base is prepared by Watson [47] as follows:

> When the sludge is removed from the drying beds it is delivered by light railway to the contractors for storage and treatment in their immense sheds, which stand on about 7 acres of ground. The sludge is broken up and spread in a thin layer on the floors of the sheds, which are so constructed that the wind can blow through them. The length of time it takes to dry depends upon the atmospheric conditions.
>
> When it is sufficiently dry it is collected and ground into a fine meal and screened so that all foreign substances are eliminated. The meal in this condition is then stored, and makes an excellent base for a fertilizer. The finely ground condition of the meal is one of the chief factors which influence its availability to the crop, as it is obvious that the finer the particles the more rapidly the agencies in the soil effect the necessary chemical and bacterial changes.
>
> Our contractors fortify it with sulfate of ammonia, bone phosphates, and sulfate of potash. It is then bagged and dispatched by rail for application to the land.
>
> The present-day cost, including working expenses and interest on capital, amounts to 19.2 cents per cubic yard of wet sludge of an average water content of 92 percent.

Van der Meulen and Smith [48] have found that the rate of filtration of ripe Imhoff sludge is greatly increased by the use of alum. Sul-

[45] *Public Works*, **51**, 355 (1921).
[46] *Eng. News-Record* **96**, 238; *ibid.* **93**, 13.
[47] *Eng. Contr.* **42**, 87.
[48] *J. Ind. Eng. Chem.* **15**, 281.

furic and sulfurous acids were less effective. The amount of alum used was 6.7 pounds per cubic yard and a cake of 80 percent moisture content was obtained in four minutes. Following these experiments, Rudolfs, Downes and Campbell [49] found that the addition of 3 pounds of alum per cubic yard decreased the draining time of ripe sludge on sand beds by one-half.

The effect of *tank depth* is to increase the solubility of gases in the liquor. A gas is practically twice as soluble under 32 feet of water as it is at the upper water surface, since it is under twice as much pressure. When sludge from a deep tank is drawn off, the pressure upon it drops to atmospheric and the mixture foams just as a carbonated beverage does when the cap is removed from the bottle. This foaming is usually attributed to "entrained" or mechanically held bubbles, while in reality it is largely due to dissolved gases released by the decrease in pressure. This foaming is obviously advantageous from the standpoint of draining.

Undigested sludge or sludge obtained by chemical precipitation is sometimes filter-pressed and heat-dried for fertilizer but this process has found only limited application, especially in America. Centrifuges have been used for fresh sludge and screenings with some success in Germany. Dumping at sea and plowing under the soil are methods which are sometimes adapted to local conditions.

The production of gas and coke by destructive distillation of sludge was suggested by some of the earlier investigators.[50] About 7000 cubic feet of gas was produced per ton of dry solids as compared with 8000 to 12,000 cubic feet from a like amount of peat or soft coal. The amount of moisture to be dealt with limits the advantage of such a method of treatment. A recent patent [51] describes a process whereby the ammonia produced by the destructive distillation of sludge is absorbed in sulfuric acid and recovered as ammonium sulfate.

From a sanitary standpoint there is little danger in using digested sludge for fertilizer,[52] although fresh sludge may frequently be the source of infection if so used.

[49] *Eng. News-Record* **91,** 888.
[50] Elsner, Spillner, and Allen, *Sewage Sludge,* p. 246.
[51] U. S. Pat. 1,499,626, January 7, 1924, Moerk, assr. to Landreth.
[52] Wolman, *Eng. News-Record* **92,** 198.

Chapter XIX.

Microbiology of Sludge Reduction.

Bacteria and protozoa have been recognized from the first as the agents most active in bringing about the degradation and stabilization of organic matter, yet little progress has been made in isolating and identifying specific organisms. The process is one which should benefit as much from thorough biological investigation as tanning, brewing, dairying and many other industries have benefited. But the small apparent chance for personal financial gain has failed to attract many investigators to this field. As a result comparatively little biological data of practical value are available.

Bacteriology.

An early investigation by Clark and Gage [1] was limited to the study of the products formed by a number of pure cultures of organisms found in sewage when cultivated on media containing various nitrogen compounds. Their results indicated that, "regarding the distribution of ammonifying and denitrifying bacteria in sewage and the effluents from sewage filters, based on a study of the biochemical functions of over 300 representative cultures from a variety of samples, it may be said that a majority of the bacteria from these sources, which are determinable by the ordinary plate methods, using gelatin as a culture medium, reduce nitrates and decompose peptone into ammonia, although these two functions are not always correlated with the same species. By the use of quantitative tests for the amount of liquefaction produced in gelatin by over 150 of these cultures, we have been able to determine approximately the relation between the peptonizing power or power to liquefy insoluble organic matter, and the ammonifying and denitrifying powers of sewage bacteria. We find that while many non-liquefying bacteria are able to reduce nitrates, or to ammonify peptone, or to do both, and many liquefying bacteria do not possess these functions, nevertheless, in a large majority of cases the possession of the first function means possession of one and usually both of the last two functions, and

[1] *Eng. News* **53**, 27; *J. Am. Chem. Soc.* **27**, 327 (1905).

the average amount of change produced in the nitrogenous matter in solution is much greater with peptonizing bacteria than with those which are unable to liquefy gelatin. Furthermore, an increase in the liquefying power appears as a rule to be synonymous with increased ability to reduce nitrates and to ammonify peptone."

In 1914 O'Shaughnessy [2] demonstrated the presence of protein-, fat- and carbohydrate-splitting bacteria in digesting sludge and noted variations between the flora of properly and improperly digesting sludge. His figures are given in Table 38.

TABLE 38.—*Bacterial Flora of Sludge.*

	Bacterial count	
	A refractory ill-smelling sludge, not digesting properly	A well-digesting sludge
	per cc.	per cc.
Gelatin plates, 20°	24,000	52,000,000
Agar plates, 37°	130,000,000	5,000,000
Coli group	7,000	60,000
Protein group	100,000	100,000+
Denitrifiers	500	100,000+
Fat-splitting organisms	10,000	100,000+
Cellulose fermenters	100,000	50,000

Söhngen [3] had previously noted the presence of a Sarcina form in methane producing sludge and Groenewege reports a micrococcus whose prevalence was proportional to the amount of methane produced. Neither of these authors demonstrated a causative relation between a specific form and methane fermentation.

A recent and extensive investigation by Hotchkiss and Murray [4] brings the bacteriology of sludge digestion pretty well down to date:

> The bacteria through whose agency some of the enzymes are produced may be divided by their physiological activity into several groups. The bacteria which were present in high dilutions of the samples, and so were considered to be abundant in the tanks, may be divided into six groups. Of these groups of bacteria those concerned with protein digestion were (*1*) the bacteria which were able to attack such a complex protein as coagulated egg albumin and produce soluble compounds, (*2*) those which attacked a less complex protein, such as gelatin, and caused liquefaction, (3) those which attacked a soluble protein, such as peptone, and decomposed it with the pro-

[2] *J. Soc. Chem. Ind.* **33**, 3R.
[3] *Loc. cit.*
[4] "The Relative Prevalence of Bacteria in an Imhoff Tank," *Am. J. Pub. Health*, **13**, 562 (1923).

duction of ammonia, and (*4*) those bacteria which also gave sulfides as a product of proteolysis.

The fifth and sixth groups are concerned with the transformation of nitrogen. There were found to be present in the tanks both those types of organisms classed as "denitrifiers" and those termed "nitrifiers." The former group consists of the bacteria which reduce nitrate nitrogen to nitrite and to nitrogen gas or to ammonia. The second group are the bacteria which produce nitrite nitrogen from ammonium salts and the coöperating bacteria which change the nitrite to the nitrate form.

In addition to these six dominant groups there have been found four groups which consist of bacteria active in the Imhoff tank but seemingly present in smaller numbers. These bacteria may be listed as: (*1*) the bacteria producing sulfate and free sulfur (from thiosulfate), (*2*) the bacteria producing hydrogen sulfide from sulfates, (*3*) the cellulose-digesting bacteria, (*4*) the bacteria which split fats.

In Table 39 the distribution of the principal organisms throughout the Imhoff tank is seen. This table is based on the average of values obtained from at least four samples, taken during the period mentioned. The albumin digesters have not been included, as figures for three samples only are available.

From this table it is seen that many bacteria are able to attack a soluble protein and from it produce ammonia. In fact, these organisms were present in the highest dilution used (1 to 1,000,000) and so the limit was never reached beyond which these organisms do not occur. Of the proteolytic organisms the gelatin liquefiers come next in abundance. The numbers of these bacteria increased in the digestive chamber over those present in the influent, while the number in the effluent was the same as that of the influent. These organisms of proteolysis were most active and increased most rapidly in the digestive chamber, seeming to indicate this place as the seat of protein decomposition.

As the prevalence of bacteria is an indication of the complexity of the protein molecule so also their numbers point to the composition of the molecule. There is less sulfur than nitrogen in the molecule and it is found that the organisms which split off hydrogen sulfide are not so numerous as the ammonifiers. Again it is in the digestion chamber where these forms which produce sulfuretted hydrogen show the most activity. The decrease of hydrogen sulfide producers is marked in the effluent and this suggests a decrease in compounds which permit of sulfide formation as the sewage flows through the tanks.

The digestive chamber of the Imhoff tank is seen as the site of putrefactive organisms which attack protein in different stages of solubility. There are more types of organisms able to utilize the partly broken down and soluble proteins than the complex and insoluble protein. The enzymes secreted by the bacteria cause the mass of suspended material to decrease by digestion, while the soluble

TABLE 39.—*Distribution of Groups of Bacteria Abundant in the Imhoff Tanks.**

	Influent	Scum	Liquid	Sludge	Effluent
	Bacteria per cc.				
Proteolytic					
Digestion of peptone with production NH_3	<1,000,000	<1,000,000	<1,000,000	<1,000,000	<1,000,000
Digestion of gelatin with liquefaction	535,000	1,000,000	775,000	775,000	550,000
Digestion of peptone with H_2S production	187,000	775,000	303,000	775,000	20,000
Denitrifiers, Reduction of nitrogenous compounds					
(a) from nitrate to nitrite	6,000	275,000	252,000	3,000	400,000
(b) from nitrate to nitrogen gas	400	272,000	251,000	50,000	41,000
(c) from nitrate to ammonia	425,000	527,000	520,000	277,000	270,000
Total denitrifiers	431,400	1,074,000	1,023,000	330,000	711,000
Nitrifiers, Oxidation of nitrogenous compounds					
(a) from ammonium salts to nitrite	200,000	525,000	30,000	252,000	21,000
(b) from nitrite to nitrate	251,000	500,000	280,000	28,000	275,000
Total nitrifiers	451,000	1,025,000	310,000	280,000	296,000

* Hotchkiss & Murray, *Am. J. Pub. Health* **13**, 562 (1923).

substances are attacked with formation of end-products, the simplest of which are such compounds as ammonia and hydrogen sulfide.

In the scum all types of bacteria showed a marked increase in numbers over the influent. This is largely due to a mechanical factor. As gas in the tanks rises it carries particles of material to which adhere large numbers of bacteria and the fat particles which eventually help form the scum also carry bacteria. This gives a large number of bacteria in the scum due to distribution and not solely to the reproduction and activity of bacteria.

Zoology.

The information concerning the animal forms which are active during sludge reduction is even more meager than that on the bacteriology. Three recent articles from the New Jersey Experiment Station represent a considerable advance in this field. From the first one[5] the following is quoted:

> Samples taken periodically, now extending over a term of six months, have shown that the Imhoff tank contains a relatively stable population composed of the minuter forms of the protozoa (the mastigophora, or flagellates). The samples examined were secured from the zones of the scum, intermediate liquid, and the sludge in process of digestion, and the organisms tabulated with regard to kind, distribution, and numbers of individuals per cubic centimeter of the material examined. The results of these analyses show that as the ciliates increase from a very few at the 3-foot level to about 900 per cc. at the 20-foot level while the flagellates are somewhat more numerous throughout and reach 1200 at the 20-foot level.
>
> The minute flagellates, in dimensions less than 30 microns, are the predominant forms of animal life, and fluctuate somewhat in numbers with respect to the acidity of the contents of the tank.
>
> The ciliate protozoa are found in fewer numbers, and are relatively much less stable in their monthly occurrence than the flagellates.

The second paper[6] is much more extensive and will be quoted at some length:

> Any study of the fauna of the Imhoff tanks must confine itself to the protozoa, for in the course of a whole year only three other animal types have been recorded. Occasionally a soil nematode is found; and there is one record of a rotifer, two records of Hydrocarinae, and one of a macrobiotus. Eggs of nematodes, encysted rotifiers, and some other forms pass through the tanks, and will de-

[5] Leon Augustus Hausman, "Preliminary Studies of the Fauna of the Imhoff Tank," *Am. J. of Pub. Health*, **13**, 562 (1923).

[6] J. B. Lackey, "Studies on the Biology of Sewage Disposal," *New Jersey Agric. Exp. Sta. Bull.* 417.

velop in cultures. But none of these forms are normal inhabitants of the tanks.

The tanks support an enormous bacterial population, which would afford a rich food for large numbers of protozoa, but other conditions tend to keep the protozoan variety down. There is also a good medium for saprophytic protozoa in the rich organic content.

Since digestion of the raw sludge takes place in the lower chamber of a tank, the protozoa living in this chamber are the ones of primary interest. It is not a large group, but rather an unusual one, for the anaërobic conditions which prevail are quite selective in their action. The effects of these conditions have been to limit the normal protozoan inhabitants of the chamber to forms which are either facultative or true anaërobes; to exclude chlorophyll-bearing organisms unless they are able to live without their chlorophyll; and to encourage a sapropelic existence. It has been found that there are: First, a small group for which the tanks offer a congenial habitat, and which thrives there. Members of this group are always met with in samples, unless some temporary change removes them, and are relatively abundant. Second, a group, members of which may succeed in holding their own for short periods of time, and may even find conditions favorable now and then for a large increase. Such forms are met with only occasionally, but sometimes large numbers of one species occur. Third, there are chance stragglers, brought in from the outside and only living for a few hours in the tanks.

The first two groups are worthy of consideration; rhizopods, flagellates and ciliates are all included. An account of those which have been found follows.

The rhizopod group is small both in genera represented and in occurrence of members. Any sample examined will usually show some small amœbas, and samples left standing, or cultured, will produce large numbers in a short time. Dimastigamœba gruberii, Vahlkampfia guttula and Hartmanella hyalina are the most numerous, but they must usually be identified by examination of prepared slides which have in the past been made from the surface film of cultured sludge or tank liquid.

The flagellate group is by far the most numerous. Sometimes enormous numbers of small flagellates are found in a tank, but often only one species is responsible for the sudden rise in the curve of population. Trepomonas agilis is the form which has occurred most frequently and in greatest numbers. It seems to increase rapidly in the tanks, at the time of and during foaming. At the end of the period of increase, the organisms swell in size and become greatly vacuolated, so that they appear distinctly abnormal; so much so, that for a long time even the genus of this type was questioned. This behavior of Trepomonas has been the most characteristic feature of the fauna of foaming tanks in the Plainfield plant. The significance of such physiological behavior is not understood, but it is certainly connected with foaming in some way. Specimens from

tanks not foaming are normal in size and appearance, and are never so numerous.

Hexamitus inflata is another small flagellate which sometimes is very numerous. It is always normal in form, however, and is a less frequent tank inhabitant. Oicomonas is commonly third; all the occurring species of this genus have never been identified. Pleuromonas jaculans is probably fourth in numbers, sometimes appearing in great epidemics. Bodo and Cercobodo are usually important in the counts. Several species of Mastigamoeba and Mastigella are common; because of their small size and relative inactivity, many of these were overlooked for a long time, but once they became familiar to the eye, were easily counted. Several different types are figured in the plates, but specific determinations for a number of them are quite impossible with available literature. Some of them are probably new species, but lack of time has not allowed sufficient observation of them to permit the naming of more than one new species.

Of the larger flagellates, none are very common. Euglena gracilis occurs more often than any other, and has abandoned its holophytic mode of life, for a saprophytic one. This is inevitable in the blackness of the tanks, but specimens kept in the light and given a medium of filtered tank liquid, do not turn green for some weeks. Three bottles of fresh solids kept in a dark closet in the laboratory for some months during experiments in digestion contained enormous numbers of colorless E. gracilis at the end.

All of the larger flagellates found thus far are Euglenoida. Euglena polymorpha and Euglena intermedia have been recorded. Entosiphon sulcatus, Notosolenus orbicularis, Menoidium incurvum and Peranema tricophorum are other Euglenoids which occur less frequently. In two tanks, Heteronema acus has been found; one of these, tank 5, is a reconstructed one, in operation for only a few months, and Heteronema seems to have found a congenial habitat there, occurring in considerable numbers.

Among the ciliata, there are only four forms which are common to all the tanks, and they are quite unusual: Holophrya, Saprodinium, Metopus, and one new genus. The Metopus is undoubtedly Metopus sigmoides, but is not the type form commonly figured, the body being usually quite swollen. No specific determination can be made for the other three forms, although an extensive search through the literature has been made. It is true that all but a few ciliates die or encyst on entering the tanks, but these have been shown to be adapted to an anaërobic existence.

Table 40 gives a complete list of all protozoa which have been found to date, in the six tanks at the Plainfield plant. It is not thought that the present list is complete. There will doubtless be additions to it from time to time, but it certainly seems to include all of the common tank protozoa, and has shown but little change in the cycle of a year. Studies up to the present would indicate that ecological factors do not vary enough to affect the organisms present, other than to cause some fluctuation of population.

TABLE 40.—*Digestion Chamber Protozoa.**

Common	Rare
Rhizopoda	
Dimastigamoeba gruberii	Amoeba proteus
Hartmanella hyalina	Vahlkampfia albida
Vahlkampfia limax	Trinema lineare
Vahlkampfia guttula	Chlamydophrys stercorea
Euglypha alveolata	
Mastigophora	
Bodo caudatus	Anthophysa vegetans
Bodo mutabilis	Bodo angustus
Bodo ovatus	Chlamydomonas sp.
Cercobodo crassicauda	Distigma proteus
Cercobodo longicauda	Entosiphon sulcatus
Cercobodo ovatus	Euglena intermedia
Clautrivia parva	Euglena mutabilis
Dinomonas vorax	Euglena polymorpha
Euglena gracilis	Heteronema sp.
Hexamitus inflatus	Menoidium incurvum
Mastigamoeba longifilum	Peranema trichophorum
Mastigamoeba reptans	Petalomonas mediocanellata
Mastigella simplex	Petalomonas carinata
Monas amoebina	Platytheca micropora
Monas minima	Salpingoeca Marssonii
Notosolenus orbicularis	Polytoma uvella
Oicomonas socialis	
Pleuromonas jaculans	
Tetramitus decissus	
Trepomonas agilis	
Infusoria	
Holophrya sp.	Aspidisca costata
Metopus sigmoides	Chilodon sp.
Saprodinium putrinum spec. nov.	Colpoda inflata
Trimyema compressa nov. gen. nov. spec.	Colpidium sp.
	Cinetochilum margaritaceum
	Cyclidium glaucoma
	Glaucoma scintillans
	Hexotricha caudatum, spec. nov.
	Lionotus fasciola
	Opercularia berberina
	Paramoecium putrinum
	Plagiopyla nasuta
	Pleuronema chrysalis
	Prorodon sp.
	Vorticella sp.

Organisms in Influent.

Vahlkampfia albida	Oicomonas socialis
Vahlkampfia guttula	Peranema trichophorum
Amoeba proteus	Pleuromonas jaculans
Amoeba radiosa	Monas minima
Trinema lineare	Aspidisca costata
Bodo caudatus	Chilodon sp.
Bodo edax	Colpoda cucullus
Cercobodo caudatus	Opercularia berberina
Cercobodo crassicauda	Paramoecium caudatum
Distigma proteus	Oxytrichia sp.
Euglena gracilis	Vorticella sp.
Oicomonas termo	

* Lackey, J. B., *New Jersey Agric. Exp. Sta. Bull.* 417.

The practical applications of these studies are pointed out by Lackey in a third paper:[7]

> The zoölogical studies have thrown some interesting light upon the numbers and activities of protozoa present. The fact that protozoa increase enormously in numbers when tanks are running badly or when foaming brought directly before us the practical question of the control of protozoa without impairing the numbers and efficiency of the bacteria. A number of experiments were made on the possibility of partially killing off protozoa, with the result that several substances have been found in the laboratory which will kill a large percentage of protozoa and at the same time stimulate the bacteria.
>
> The absolute relation between overload and faunal conditions is shown clearly as a result of surveys of tanks throughout the past year. Tank 3 showed serious cases of foaming in July, in early September, in late September, and in early October. Late in October it foamed over, and continued to do so until about November 7 when the foaming subsided for a short time. Then after a few days it began to foam again, and did not stop until the first part of June, 1925. This tank was in operation at all of these times, and the periods when the foaming subsided were periods when the tank was resting. It was continuously in operation from early November to June. In June, all of the sewage was diverted to flow first through Tank 1, then through the other tanks. Tank 1 retained 86 percent of the solids and the flow through the next tank took out only a small percentage. It is seen that Tank 3 thus received a very small amount of fresh solids compared to what it had previously received. The effect was instantaneous; foaming subsided. Just how successful this is remains for the plant superintendent to say, but the immediate effect is explanatory.
>
> The fluctuation of the protozoan fauna in this tank follows the working and resting periods almost exactly. Not only is this true for 1924-25: between December 1 and May 31 of the preceding year, five bad cases of foaming showed five large increases in protozoa and when foaming became permanent in Tank 3 the protozoa climbed to high levels and stayed there. One peak was over 500,000 per cubic centimeter of liquid. Once or twice the numbers receded to rather low levels, but this did not last long. Toward the end of this period in April and May, Metopus became so numerous in this tank that the liquid might have been taken for a laboratory culture of the animals.

Tank	Condition	Protozoa per cc.	Date
3	Not foaming	19,000	October 18, 1924
4	Foaming	345,000	February 13, 1925
4	Not foaming	0	May 14, 1925
4	Foaming	51,000	June 3, 1925

[7] "Studies on the Biology of Sewage Disposal," *New Jersey Agric. Expt. Station, Bulletin 427* (1924-1925).

The percentage of CO_2 shows as decided a fluctuation as the animal population, and its peaks come at about the same time. Part of this effect is probably due to the bacteria, with the probable result that the pH values are partly lowered by the living organisms instead of being a limiting factor for them.

In tanks containing large numbers of protozoa the dry matter contains a much lower percentage of ash than in tanks where there is a small fauna, as is shown in the following analysis made on February 13, 1925:

Tank	Protozoa per cc.	Weight Liquid per cc.	Dry Solids Percent	Ash Percent
3	345,000	1.090	0.82	11.1
5	22,000	1.092	0.90	45.0

The extra amount of organic matter is hardly accounted for by the bodies of the protozoa themselves, since protoplasm is largely water, but must represent food. This phase of the subject decidedly requires investigation.

Summary.

A recheck of data advanced in previous years strengthens the conclusion that the vertical distribution of ciliates is variable, and that the maximum occurrence of flagellates is near the point where the slots in the tanks occur.

No seasonal fluctuation of protozoa is evident for species, genera, ciliates, or flagellates.

There seems to be a direct relation between chemical end-products and animal population present, for when large amounts of CO_2 are present large numbers of protozoa occur. This affords some explanation for the fact that protozoa increase with the opening and decrease with the closing of a tank.

In 5 out of 6 tanks, every time foaming occurred there was a large increase of protozoa. When Tank 3 foamed continuously, the protozoa reached numbers comparable to those found in activated sludge.

Accumulation of partly digested material results in large increases in numbers of protozoa.

The protozoa are independent of short ranges of pH values above or below 7.0 in the tanks.

Tank protozoa are largely independent of bacteria as a direct source of food: they are for the most part sapropelic; they may utilize bacterial decomposition products. This can be related to the correlation between the distribution of solids and the distribution of protozoa.

The tank protozoa are either facultative or obligatory anaërobes that may be cultured in the laboratory.

Other Imhoff tanks which have been investigated have the same genera of protozoa as at Plainfield.

Chapter XX.

Removal of Colloids from Sewage by Filters

The effluent from a well-designed settling tank still carries sixty-five percent or more of the putrescible matter with it. This organic matter is largely in a colloidal state of dispersion although some is in true solution and some in suspension. A further coagulation and clarification occurs when this liquor is held for a week or more but the improvement is not sufficient to warrant such treatment. Alum or copperas as coagulants are effective but produce a large amount of objectionable sludge. It was early recognized that the colloids could be quickly and effectively removed by means of contact surfaces if aërobic conditions were maintained to a certain degree.

Types of Contact Surfaces.

An outline or suggested classification of the various types of contact surfaces is given in Figure 48. (*See also* Chap. XV.) The slow sand filters, earth filters and sewage farms were the earlier developments. Their action is more nearly true filtration (*see* discussion of action of water filters). The coarser grained types of surfaces are of more recent development. Several of the types listed in the classification have not passed the experimental stage. The sprinkling filters and contact beds are widely used and there are a large number of activated sludge plants in use. The Travis colloiders have been installed in a number of tanks and there are now five installations of Imhoff's Tauchkörper (contact aërators) in use in Germany. Imhoff [1] points out that there is a loss of head through all of those types in which the active surfaces are exposed to the atmosphere while that is not the case with immersed surfaces like activated sludge, Tauchkörper, etc.

The effect of these contact surfaces is to remove the colloidal organic matter leaving a practically clear liquid. At the same time a certain amount of oxidation occurs as the result of which carbon dioxide and nitrates are formed.

[1] *Fortschritte Abwasserreinigung* (1926).

Theory of Action of Contact Surfaces.

Two opposing theories have been suggested for the explanation of the reactions taking place during the removal of colloids by contact surfaces. One might be called the Physicochemical theory of Travis—

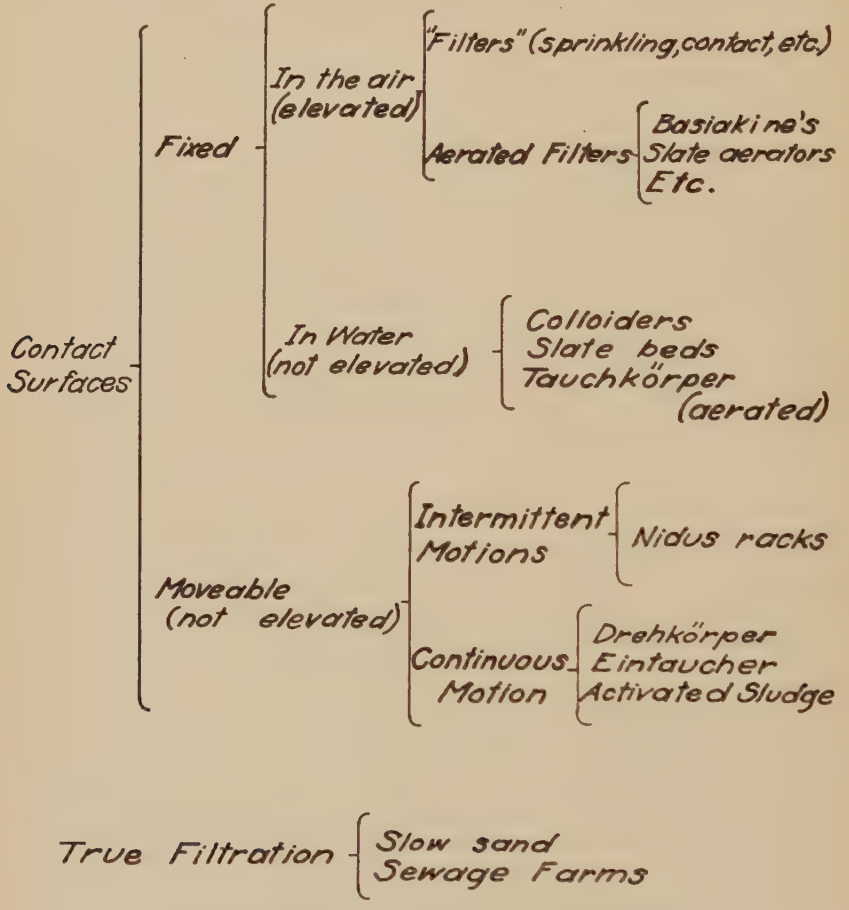


FIG. 48.—Devices for Treatment of Settled Sewage.

the Hampton Doctrine—and the other the Biochemical theory of Dunbar. Ardern [2] summarized these two theories as follows:

The earliest theory advanced with respect to the mechanism of the purification changes effected by the "filtration" of "sewage" was

[2] *Second Rept. on Colloid Chem. to the Brit. Assoc. Adv. Sci.* 1921, p. 81.

based on the work carried out at the Lawrence Experimental Station, Mass., in respect of the development of the intermittent sand filters as advocated by Frankland, as a practical means of sewage purification.

According to this theory, the suspended solids applied with the sewage or tank effluent are arrested mechanically in the filter by virtue of its fine pores, and subsequently oxidized, and the organic matter in solution is directly oxidized and mineralized by bacterial agency during the course of its passage through the filter with the accumulation within the filter of small quantities of "humus," which is very resistant to further fermentation. Presumably colloids are included in the organic matters in solution, although they are not referred to specifically.

This simple representation of the purification process received almost universal support, notably by Stoddart as recently as 1909.

Dunbar assumed that it was not possible to bring about the complete oxidation of the complex organic matter present in solution in sewage during the short period of time taken by the liquid in passing through the filter, and as the result of a series of experiments extending over a considerable period (1897-1900) carried out by him and his colleagues at the Hamburg Hygienic Institute (vide "Principles of Sewage Treatment") he advanced what is known as the "absorption theory" of sewage purification.

This theory explains the mechanism of the purification changes as follows:

1. The actual suspended matters are removed by attraction of the filtering media, etc.
2. The dissolved matters (true and pseudo solution) are retained by absorption phenomena, which is accelerated and increased as the slimy matter, or what is termed the bacterial film, accumulates on the media as the filter becomes mature.
3. The matters thus retained are oxidized by chemical action (condensed oxygen, etc.), and by the agency of bacteria and higher forms of life. The resultant soluble product—mineral salts, amino-acids, etc.—are subsequently washed out of the filter by succeeding quantities of sewage treated.
4. This absorption process is prevented from ceasing by the action of microörganisms, etc., in the presence of atmospheric oxygen.
5. There is a residue of organic matter, etc., which is very resistant to further oxidation changes, which either accumulates in the filter or is discharged with the effluent.

It will be noted that this theory draws no distinction between matters in true and pseudo solution so far as the mechanism of the purification changes is concerned.

Experience with the operation of the Hampton sewage works, where relatively large quantities of sludge accumulated in the filtra-

tion area, led Travis to study the question of sewage colloids in relation to sludge production. As the result of a series of experiments carried out in conjunction with Johnston, he advanced in 1905 what is known as the Hampton Doctrine.

According to this theory the purification process is primarily and essentially a de-solution effect brought about purely by physical causes and any bacterial or biological action is definitely ancillary.

Unlike Dunbar's theory, a distinction is drawn with regard to the mechanism of the purification process as between organic matter in colloidal solution and matter in true solution.

It is held that whereas "organic matters and products in actual solution, e.g., ammonia, sulfuretted hydrogen and volatile products, are absorbed by the accumulated deposits in the filter," the solids in colloid solution are coagulated or precipitated "in virtue of a physical action"—effect of extended surface contact, etc.

These coagulated colloids are either retained in the filter or discharged with the effluent from the filter, and any biolytic action on them is a very slow and prolonged process, and consequently in addition to the actual suspended solids in the sewage or tank-effluent treated, the amount of such coagulated colloids, which have been termed "ultra sludge," must receive attention in considering the amount of the total sludge to be dealt with.

In discussing these theories, it is proposed to confine attention as far as possible to the purification effect on matters in colloidal solution.

Briefly, it may be said that—

(1) In the earlier theory, especially as propounded by Stoddart, such matters are held to be oxidized directly by bacterial agency during the passage of the liquid through the filter.

(2) Dunbar's theory provides for their preliminary absorption by the filtering media and the gelatinous coating thereon, with subsequent more or less rapid oxidation by agency of condensed oxygen, bacteria and higher forms of life.

(3) According to the Hampton Doctrine, such absorptive processes are confined to the matters in true solution, and the matter in pseudo solution is coagulated by virtue of a physical action. The subsequent biolytic oxidation of the matter thus deposited is a very prolonged process.

In connection with the question of absorption, it may be mentioned that Clark, and later Clifford, have demonstrated that the mean time of passage of sewage through a filter as operated in practice, while it varies considerably, dependent on several factors, is, on the whole, much longer than the few minutes spoken by Dunbar, and may in some cases amount to more than one hour, which would allow time for appreciable bacterial action.

Also that Harriette Chick, Fowler and Gaunt, and Stoddart have shown that absorption of ammonium salts does not take place under sterile conditions except with material such as clinker, etc., which

allows of chemical interaction between the liquid and the media. Stoddart has extended this observation to solutions of albumin and was unable to confirm Dunbar's experiment which showed 50 per-cent loss of albumin. He suggests either preliminary decomposition (prior to use) with formation of ammonia which would be partially fixed by the clinker, or direct chemical interaction as a possible explanation. It is obvious that experiments designed to show purely absorptive phenomena should be carried out with material entirely inert, such as pure quartz as used by Fowler and Gaunt.

Stoddart's conclusion that there is no evidence of the preliminary absorption of the soluble constituents of sewage was based on the results of his experiments on the nitrification of solutions of (*a*) ammonium salts, (*b*) urea, (*c*) albumin and (*d*) sewage deprived of its suspended matter by filtration through paper, in which the flow through his experimental filter (seeded with a vigorous growth of nitrifying organisms) was interrupted from time to time, and the liquid treated replaced by salt solution of known strength applied at exactly the same rate.

The coincidence of a series of curves plotted with respect to the time taken to attain maximum nitrification and maximum chloride content was claimed to establish that preliminary absorption did not take place.

Stoddart also objects to the absorption theory, developed as it was as the result of studies with contact beds, being applied to the modern percolating filters where the conditions differ very considerably. On the other hand, Dunbar considers that such altered conditions are more favourable to absorptive phenomena.

For a full discussion of the difference between the theory of preliminary absorption of colloidal matter and of its direct coagulation and deposition in the filter, the reader is referred to a paper presented by Travis to the meeting of the Association of Managers of Sewage Disposal Works at Leicester (July 4th, 1908), which appeared in the July 10th, 1908, issue of the *Surveyor*, and the discussion thereon which ensued between the author and Lubbert, of the Hamburg Hygienic Institute.

So far as the mechanism of the preliminary removal of the matter in colloidal solutions is concerned, both Dunbar and Travis agree that it is essentially the result of physical action; mention should therefore be made of the work of Fowler and Mumford. They found that under strictly aërobic conditions, a bacterium isolated from a body of water receiving colliery discharges, acting through its enzyme in the presence of small quantities of iron salts, was capable of coagulating sewage colloids in the course of a few hours. Such removal of colloid matter from pseudo-solution is effected without the aid of surface contact other than is provided by the air bubbles and the matter precipitated.

The evidence available with respect to the mechanism of the removal from sewage of organic matter in pseudo-solution may be summarized thus:

(I.) The experiments of Stoddart designed to show its direct oxidation by bacterial agency cannot be considered conclusive. On the other hand it has not been demonstrated that under the favourable conditions present in an efficient filter, in which the sewage passes in thin films over a net work of media covered with an active bacterial slime, the mean time of passage is insufficient to allow of direct biolytical oxidation of some portions of the organic matter in pseudo-solution.

(II.) While it is accepted that sewage colloids may be precipitated or coagulated by intimate surface contact, this de-solution theory can scarcely represent the whole phenomena of colloid removal otherwise such action would continue in the absence of microörganisms.

(III.) The conditions met with in a mature and efficient filter are such as to render it most probable that absorption phenomena play an important part in the removal of matters from pseudo-solution.

In considering the final fate of the matters removed from pseudo-solution during the purification process it may be said that, independent of what may occur with experimental filters inoculated with vigorous growths of microörganisms, and operated under ideal conditions, Stoddart's view that none of the solid matter retained in sewage filters is derived from organic matters originally in pseudo-solution is not consistent with what obtains in actual practice.

On the other hand the contention of Travis that the retained colloids undergo very little change as the result of biolytic action was formulated on entirely inconclusive evidence.

In this connection mention may be made of Dunbar's experiment in which a solution of albumin containing nitrogen equivalent to the organic nitrogen content of an average sewage was applied to a mature filter, with the result that almost quantitative oxidation of the sulphur was obtained, while 58 per cent of the total nitrogen appeared in the filtrate, 10 per cent as ammonia, 20 per cent as nitrate and 25 per cent as organic nitrogen. Thus 42 per cent of the nitrogen disappeared either in the gaseous form or accumulated in the "humus." A considerable part of the carbon of the albumin also disappeared as gaseous carbonic acid, but a part also went to form the "humus" which accumulated in the filters.

It would thus appear that the nitrogenous organic constituents of sewage whether in actual suspension or in colloidal solution are more or less equally amenable to biolytic action, and consequently the percentage resolution of total organic matter observed in connection with the sand filters treating crude sewage should apply fairly well to the matters coagulated from pseudo-solution.

In conclusion it is evident that the total unresolved organic matter either retained in the filter or discharged with the effluent, will depend on the character (suspended solids and colloid contents) of the sewage treated and the rate of application with respect to the capacity of the filter, which will vary according to the type employed.

Development of the Sprinkling Filter.

The sprinkling filter, because of its wide use and demonstrated effectiveness, deserves discussion at some length. Its development has been traced by Strickhouser [3] of the Illinois State Water Survey Laboratory, from whom we shall quote:

> About 1865 Dr. Alexander Mueller,[4] a well known chemist of Berlin, showed that sewage could be purified through digestion and mineralization by microörganisms. His experiments, however, did not meet with such lasting success as did the classical ones of Sir Edward Frankland [5] in 1868. Frankland set up filtration experiments in the laboratory, using glass cylinders six feet high and about ten inches in diameter, open at the top and bottom and placed over earthenware troughs. A glass tube was inserted in the middle for aëration purposes. Five different filter media were used; coarse gravel, sand, soil, loamy marl and peaty soil. The filters were dosed morning and evening with crude London sewage applied at different rates. After four months of successful purification, Frankland laid down the well-known principle of "intermittent filtration," namely, that natural land or artificial filters do not clog if the sewage is applied in small doses and allowed to trickle away before the application of the next dose. So favorably were the Royal Commission impressed with the results that they recommended intermittent land filtration as a satisfactory method for the treatment of sewage.
>
> After a series of thirty-eight unsuccessful experiments by English towns on this method of land filtration it seemed probable that Frankland's observations were soon to be forgotten. It was not recognized at that time that the failures recorded were due to the use of unsuitable land, overloading, or inadequate resting and aëration.
>
> In 1886, the Massachusetts State Board of Health was granted the power to study the general question of stream pollution and sewage treatment. For this purpose, an experiment station was established at Lawrence in 1887. Their studies showed the correctness of Frankland's early views and furnished much valuable data on the theory and operation of the intermittent sand filter. Just as Frankland's experiments may be regarded as forming the foundation of natural biological methods of sewage treatment, so may the early work of the Lawrence Experiment Station be regarded as forming the basis for modern artificial biological methods.
>
> After studying the intermittent sand filter at Lawrence, it was thought desirable to find a method for obtaining higher rates of filtration and a decrease in surface clogging and accumulation of solids in the bed. As a beginning in this direction, two gravel filters, each being one twenty-thousandth of an acre in area and about five

[3] *Relation of Depth of a Sprinkling Filter to Degree of Purification.* Thesis Univ. of Ill., 1926.

[4] Fuller, p. 616 (1912).

[5] *First Report River Pollution Commission (British)*, (1868).

feet deep, were constructed and put into operation in June, 1889.[6] The stones used in one of these filters were of such size that they would pass through a mesh 0.375 inch square but not through a mesh 0.125 inch square. The stones used in the other filter were somewhat larger, being of such size that they would pass through a mesh 1.25 inches square but not through a mesh 0.75 inch square.

Sewage was applied to one of these filters, Number 16A, at the average rate of 70,000 gallons per acre per day for a period of four months. This rate was secured by the application of sewage to a depth of about one-third of an inch on the filter surface at hourly intervals for nine hours a day. Nitrification became very active in less than four weeks and during the entire period of operation the nitrates in the effluent averaged 10.6 parts per million.

The results obtained in the operation of these small filters led to the observation that purification of sewage by nitrification, and the removal of bacteria, is not mechanical to any great extent. This had been suggested in the case of the sand filter, but it was not so clearly demonstrated as with a filter of coarse gravel. With such material, the possibility of straining through fine pores is practically eliminated. The essential feature of filtration through a coarse medium, as stated in the Lawrence reports, is "the slow movement of the liquid in films over the surface of the stones in contact with air."

The adoption of coarse gravel as a filtering medium made it necessary to find a new means of distributing the sewage over the bed. With the sand filters, sewage was allowed to flow onto the bed and distribute itself by flooding the entire filter. With gravel filters, sewage did not spread out over the surface, but passed directly downward through the large voids without being purified. It was early determined[7] that without effective distribution at the surface the sewage could not percolate through the bed in films; instead, it would rush downward in large volumes in some parts of the filter and not reach other parts. The earliest means used for securing equal distribution over such a filter was an automatic siphon discharging upon a dash-plate on the surface of the filter, described by the Lawrence Experiment Station[8] in 1891. The device gave fairly satisfactory results on the small experimental filters, but was impracticable for any large installation.

In 1891, C. E. Waring, Jr.,[9] patented a filter which required forced aëration. A top layer of fine gravel placed over the coarser material of the filter was used to secure even distribution by causing the sewage to flood the top of the bed. The fine surface layer hindered the natural aëration of the filter and for this reason it was necessary to blow air up through the bed. To use Waring's words in

[6] *Purification of Water and Sewage*, Mass. State Board of Health Special Rept., 1890, p. 549.
[7] *Opus cit.*, p. 25.
[8] *Mass. State Board of Health Rept.*, 1891, p. 555.
[9] *The Purification of Sewage by Forced Aëration*, Newport, R. I., 1895.

describing the process, "the sewage trickles down in a thin film over the surfaces of the particles of coke or other filtering material, while through the voids between the particles, and in immediate contact with the trickling films of liquid, a current of air is constantly rising, being introduced at the bottom of the tank by a blower." His filter successfully purified the effluent from a preliminary strainer at the rate of 800,000 gallons per acre per day. The principle of oxidation of the organic matter employed in this filter is undoubtedly correct; the means of attaining this end, however, are rather involved and need close attention. A large-scale installation at East Cleveland, Ohio, had to be abandoned because of clogging and imperfect purification.

At this point, a brief mention will be made of the development of artificial biological methods in another direction. At Barking, England, Binnie, Crimp, and Dibden[10] constructed a coke breeze filter three feet deep and covered with a three-inch layer of gravel. After unsuccessfully operating this filter by intermittent-continuous dosing, they obtained good purification on the fill and draw basis. This method of operation, known as contact filtration, has not been so generally adopted because the rate of filtration is only half that which can be obtained with the sprinkling filter and hence requires more area than the latter method. Contact filters are used to some extent for small installations where their comparative freedom from odors, and their ability to operate on a small head are real advantages.

Dibden,[11] after some experimentation on contact filtration, constructed his well-known slate bed for the aërobic treatment of sewage. He claims that his bed will go far in reducing the amount of sludge obtained from sewage by aërobically and inoffensively digesting it on the slates where it is originally deposited. These slate beds have not been adopted very generally because the additional removal of material does not seem to be at all commensurate with the cost of construction.

Lowcock,[12] in 1892, filtered the effluent from a chemical precipitation process at Malvern through a gravel filter at the rate of 300,000 gallons per acre per day. He also used a fine surface layer of gravel to distribute the sewage. Hence in order to maintain aërobic conditions, compressed air was forced into the lower layers of the filter through perforated pipes. A satisfactory effluent was produced, but the cost of compressing the air was too high to warrant extensive adoption of this type of filter. Furthermore, a very serious objection to this and to Waring's filter is the difficulty of securing an even distribution of air throughout the entire filter bed.

In 1892, the Lawrence Experiment Station[13] constructed two gravel filters using a forced downward draft. Sewage was applied

[10] Dunbar, W. P., *Principles of Sewage Treatment*, 1908.
[11] *Op. cit.*
[12] Lowcock, S. R., "Experiments on the Filtration of Sewage," *Proc. Inst. Civ. Eng.* **115**, 297 (1893).
[13] *Mass. State Board of Health Rept.*, 1893, p. 422.

at the rate of about 500,000 gallons per acre per day. Two similar filters were constructed in 1895 [14] and operated at rates of 698,000 and 1,000,000 gallons per acre per day. Good nitrification was obtained and the effluents were stable. During the course of the experiments, the amount of aëration was gradually reduced until a minimum of two hours aëration a day was reached. The principle of forced aëration was abandoned later and all subsequent filters were built to receive only natural aëration.

In 1893, J. Corbett,[15] borough surveyor of Salford, England, was confronted with the necessity of finding some means of treating the sewage of the rapidly growing population of that industrial town. As neither irrigation nor land filtration could be adopted, he turned to artificial filtration for a solution to his problem. He based his work on the early Lawrence experiments which verified Frankland's principle of allowing the liquid to trickle away freely. He also realized the importance of even distribution of the sewage and hence directed all his efforts towards finding the most satisfactory method for sewage distribution.

Corbett first used wooden troughs for distributing the sewage. Later he raised these troughs several feet above the surface of the bed to let the sewage fall on the filter in a shower. He also constructed a filter in several units, or layers, having air spaces between the layers. The sewage in passing through the filter dropped from one of these units to the next in the form of a rain. These filters did not seem to give as satisfactory results as those having the filtering medium in one compact body. Still later he used rotating sprinklers and late in 1894 he adopted the fixed spray jet which has become the most widely used method of distribution for sprinkling filters.

At about the same time that Corbett began his experiments in 1893, F. Wallis Stoddart [16] of Bristol described an apparatus for purifying sewage, based on the trickling of sewage over coarse material with natural aëration. He exhibited his apparatus before the British Medical Association in 1894. It consisted of two burettes filled with coarse chalk and placed one directly under the other. The sewage was allowed to drip on the chalk in the upper burette and trickle successively through the two burettes. Sewage so treated was completely nitrified when applied at a rate of 1,200,000 gallons per acre per day and was well purified at a rate of 5,800,000 gallons per acre per day. A solution containing 140 parts per million of nitrogen in the form of ammonium sulfate was almost completely nitrified using a rate of 11,600,000 gallons per acre per day.

With only a small but constant trickle of sewage falling on the coarse chalk, the interstices were never filled with sewage to the exclusion of air. The sewage percolated in thin films over the chalk, always in contact with the interstitial air. These were the precise

[14] *Mass. State Board of Health Rept.*, 1895, p. 465.

[15] A dozen years of sewage purification experiments on a large scale at Salford, England, *Eng. News* **49**, 191 (1903); see also *ibid.* **48**, 155 (1902).

[16] Water Analysis—the interpretation of results, *Analyst*, **19**, 39 (1894).

conditions which the Lawrence Experiment Station had proved to be essential in continuous filtration. Stoddart pointed out that the exceptional activity of his filter was due to the regular and continuous flow combined with perfect aëration.

Stoddart maintained that Frankland's principles alone formed the basis of his filtration experiments and that he was in no way influenced by the work of the Lawrence Experiment Station. He even asserted that the Massachusetts data had been of no importance in the development of the coarse-grained filter. This statement has been refuted, however, by Dunbar,[17] who gives proper credit to the Lawrence work. Stoddart's claim on priority in continuous percolating filtration cannot be upheld, for Corbett's experiments were well under way in 1893 when Stoddart published his first paper. By continuous percolating filtration is meant the filtration of sewage through a coarse medium at relatively high rates. This term is used in opposition to intermittent filtration where the sewage is applied to the land or sand at intervals of a few days. In the so-called continuous filtration the sewage is applied to a coarse medium at intervals of only a few minutes.

In 1899 Stoddart constructed a large filter at Horfield, using corrugated perforated plates to effect distribution of the sewage. Sewage flowed through the holes in the plates and thence along the under surface until it reached numerous small projections, from the lower points of which it fell on the bed in drops. The distribution and purification were good, providing the plates were perfectly level. The difficulty of keeping the plates level and of preventing growths in the perforations renders this method of distribution of doubtful practical value.

Dunbar [18] in 1901 worked out the so-called Hamburg type of trickling filter for the treatment of small amounts of sewage obtained from institutions. He used twenty inches of 0.04- to 0.12-inch material on top, then four inches of 0.12- to 0.4-inch material, and then four inches of 0.4- to 1.2-inch material over the coarse material of the filter. The distribution is effected by this fine layer of material and clogging can be remedied by occasionally turning over the upper six inches with a shovel and resting the bed for a day or two.

Many other devices have been suggested for distributing the sewage over a filter. Most of them have not been widely adopted in this country and will only be mentioned to show the trend of experiments in this field. Carfield in 1896 used fixed perforated pipes fed by a siphon. Later the pipes were made movable: first, about a center and finally to cover a rectangular area. Whittaker and Bryant in 1898 used rotary sprinklers fed by a pulsometer which also served to warm the sewage. They attached much importance to the heating of the sewage but later experiments at Leeds have shown that heating has no advantages. Candy in the same year used a rotary

[17] *Op. cit.*
[18] *Op. cit.*

sprinkler differing from the previous one by being fed from a vessel at the junction of the distributing arms.

Mather and Platt used open rotating troughs in an attempt to avoid the shortcomings of perforated pipes. Scott-Moncrieff used a motor-driven rotating open trough. Although the distribution was excellent, the cost was prohibitive. Travelling distributors operated by electricity or by overdriven water-wheels have been used to some extent in England.

Ducat built a filter having walls of nearly horizontal drainpipes to aërate the bed. In addition to providing for as complete aëration as possible, he supplied external heat to aid in the purification.

Such, in brief, has been the gradual evolution of the sprinkling filter as we know it today. The principle was discovered by Frankland; the coarse-grain filtering medium was introduced by the Lawrence Experiment Station; and the fixed spray jet was invented by Corbett.

Theory of Purification by the Sprinkling Filter.

The effluent from a sprinkling filter presents a marked contrast to the sewage with which the filter is treated. The improvement makes itself evident first of all by the appearance of the samples. The settled sewage applied to the filter is quite turbid and milky in appearance, whereas the settled effluent is clear and almost free from turbidity. The effluent contains at times about as much suspended matter as the sewage itself, but of an entirely different character. The brownish flocculent material in the effluent settles out quite readily, leaving the supernatant liquid clear. Sewage solids, on the other hand, will not settle because of their colloidal nature, and are hard to remove even by laboratory filtration methods. Lederer [19] has found that the finely divided, slow-settling suspended matter and pseudo-colloidal matter cause most of the putrescibility of raw sewage. The chemical nature of the effluent solids is such that they are far more resistant to biological decomposition than the fresh sewage solids.[20]

Chemical analyses of the sewage and effluent reveal still greater differences in the character of each. The raw sewage shows relatively large amounts of free ammonia and albuminoid nitrogen, organic nitrogen and "oxygen consumed." Nitrates, nitrites and dissolved oxygen are present in very small amounts, if at all. On the other hand, the settled filter effluent is low in free ammonia and albuminoid nitrogen, organic nitrogen and oxygen consumed. Nitrates, nitrites and dissolved oxygen are present in fairly large amounts. These conditions give to the effluent its "stability," or resistance to putrefactive decomposition.

[19] Lederer, A., "The Relation of the Putrescibility of the Settling and Non-settling Suspended Matter in Sewage," *Eng. Rec.* **64**, 733 (1911).
[20] *Mass. State Board of Health Rept.*, 1891, p. 454.

Mumford [21] explains the mechanism of nitrification by the oxidation of ammonium salts in several stages. Hydrogen atoms are successively hydroxylated, with the subsequent elimination of water from the molecule. In support of this theory, he has found hydroxylamine salts and salts of hyponitrous and nitrous acid in the reaction mixture during such an oxidation. Any nitrogen loss as gaseous nitrogen is due to the inter-action of the intermediate products. Furthermore, since the relative concentration of these intermediates is dependent upon aëration, we have an explanation of the differences in nitrogen losses from contact and sprinkling filters.

Clark and Adams [22] have shown that nitrification ceases when the carbon to nitrogen ratio in the sewage becomes too great. Good purification and production of a satisfactory effluent can be secured, nevertheless, if the filter is gradually accustomed to such sewage by the application of increasingly larger doses.

Rudolfs,[23] however, states that in all probability denitrification goes on continuously and simultaneously with nitrification in a sprinkling filter, but becomes apparent only when it exceeds the latter. This occurs in the spring just before the bed begins to "unload."

Concepts of the Mechanism of Purification.

In the light of recent developments in the field of colloid chemistry, it is felt that certain of the phenomena in the purification process can be explained on a more rational basis. The correct interpretation of the phenomenon of adsorption will undoubtedly throw much light on the mechanism of purification, and as W. C. McC. Lewis says, "There can be no doubt that more complete information of this purely physical phenomenon is the first step towards a rational understanding of the more complicated phenomena of the dye-house and the filter-bed." It is believed that such indefinite terms as "enormous pressures" and "absorption" used by Dunbar, and such vague terms as "de-solution" and "physical forces" used by Travis can be replaced by a more exact analysis of the fundamental principles underlying the whole process of purification.

As postulated in the older theories, coarse suspended solids are arrested and held by the slimy bacterial film. Such action is attributed to the gelatinous nature of this growth and to the formation of fine pores by adjacent films, through which large particles cannot pass. However, the growth which accumulates in a mature filter is characterized by an extremely large surface area, and hence exhibits,

[21] Mumford, E. M., "The Mechanism of Nitrification," *Proc. Chem. Soc. (London)*, **30**, 36 (1914).

[22] Clark, H. W., Adams, C. O., "The Influence of Carbon upon Nitrification," *J. Ind. Eng. Chem.* **4**, 272 (1912).

[23] Campbell, F. L., Rudolfs, W., "Studies on the Biology of Sewage Disposal," *Rept. of Sewage Substation with N. J. Agric. Exp. Sta., Bull.* **390**, 28 (1923).

to a maximum degree, the surface phenomenon of adsorption, which will be discussed later.

Gibbs [24] has determined from thermodynamical considerations, that, when a change in surface tension takes place due to the formation of a solution, a change in concentration also occurs, the surface film having a different concentration from the main portion of the solution. Film concentrations tend to change so as to decrease surface tension. In other words, if a solute increases the surface tension of the solution, the film will be more dilute than the main portion of the solution; if it decreases the surface tension, then the solute will concentrate in the surface film. The rule is expressed mathematically by the equation: *

$$C = -\frac{c}{RT} \cdot \frac{ds}{dc}$$

Thus, when the surface tension decreases with increasing concentration of solute, $\left(\frac{ds}{dc}\right)$, the concentration of solute, (C), in the surface layer is positive and hence greater than in the main body of the solution.

Most salts and all strong bases increase the surface tension of water; but ammonia and nitric and hydrochloric acids decrease it.[25] Gibbs' rule applies only to substances in true solution, but a similar phenomenon has been found to occur in colloidal solutions. Many substances like soaps and proteins form colloidal solutions which have lower surface tensions than pure water.[26] Ramsden [27] found such substances to concentrate in the surface film. Our interest in these substances arises from the fact that such organic material must be removed from sewage in order to destroy its putrescibility. It has been shown by Willows and Hatschek [28] that surface concentrations of such colloids as Congo red, methyl orange, etc., are twenty to one hundred times as great as those calculated from the formula. No expression has been derived to cover the behavior of colloids in this respect.

In sewage, we have colloidal soaps and proteins which tend to concentrate in a surface film as pointed out above. This need not be only the air-liquid interface, but can be the interface between the bacterial jelly and the sewage. For example, Donnan and Lewis,[29] in using oil drops to measure surface concentrations of colloids, ob-

[24] Gibbs, J. Willard, *Scientific Papers* **I**, 219 (1906).

* This simplified form of the Gibbs equation is true in a qualitative sense only.

[25] Landolt-Bornstein, *Physikalisch Chemische Tabellen.*

[26] Quincke, *Physico-chemical Tables,* 1911.

[27] Ramsden, W., "Abscheidung fester Korper in den oberflachen-schichten von Lösungen und 'Suspensionen,'" *Z. physik. Chem.* **47**, 336 (1904).

[28] *Surface Tension and Surface Energy,* p. 46 (1915).

[29] Lewis, W. C. McC., "An Experimental Investigation of Gibbs' Theory of Surface-concentration, Regarded as the Basis of Adsorption," *Phil. Mag.* **233**, ser. 6, **17**, 466, 1909, see also *ibid.* **231**, ser. 6, **15**, 499 (1908).

tained some results which showed large discrepancies from the calculated figures. They ascribed this to colloidal gelatinization or flocculation on the oil surface and stated that it may be regarded as excessive adsorption due to the marked lowering of the surface tension, resulting in the overstepping of the solubility of the solute and the consequent flocculation on the surface layer.

The substances which concentrate at the jelly-sewage interface are attacked by the bacterial and biological life of the jelly. As rapidly as these substances are removed by digestion, others come to the interface until the surface tension is reduced to its previous value. Thus a dynamic equilibrium is maintained between the removal of organic matter from the interface by digestion, and the addition of more organic matter to the interface by virtue of surface tension lowering.

Soluble products, such as ammonia, which lower the surface tension of water, obey Gibbs' rule closely and therefore concentrate at the interface. Because of their solubility, they may also be removed by direct preferential absorption into the living cells present in the jelly.

The bacterial film or jelly always contains dissolved and probably adsorbed oxygen, obtained chiefly from the air drawn into the bed, but to some extent from that dissolved in the incoming sewage. In the presence of oxygen, bacterial and biological agencies decompose the organic matter with the final production of nitrate, carbon dioxide and a humus-like residue. It is certain that enzymes play an important part, at least in the initial states of the decomposition of proteins.[30] Nitrates, being salts, raise the surface tension of water and are therefore driven away from the interface into the main body of the liquid and thus pass out of the filter. The humus remains on the stones and materially increases the effective surface. Salts like sodium chloride pass directly through without being adsorbed, since they raise the surface tension of water and do not concentrate at the interface. The fallacy of using sodium chloride to determine the detention period of organic matter in a filter will be more fully discussed later.

The ammonia originally adsorbed from the sewage, together with that formed in the decomposition of protein by bacterial activity, may undergo at least one of several fates. It may be used in the formation of living protoplasm by bacterial cells; it may be oxidized to nitrates by bacteria in order to meet energy requirements; it may be oxidized by organized or unorganized catalysts. When the adsorbed ammonia and oxygen meet on the film, we have conditions similar to those existing in the oxidation of organic substances in the presence of a catalyst possessing enormous surface area. It is not unreasonable, then, to postulate the catalytic oxidation of ammonia on the bacterial film. Since the amount of nitrate in the filter effluent represents only about fifty per cent of the ammonia in the sewage

[30] Thompson, J. W., "A Study of the Biology of the Sprinkling Sewage Filter," *New Jersey Agric. Expt. Sta. Bull.* **352,** 25 (1921).

it is evident that the difference between the sum of the nitrate and ammonia in the effluent and the ammonia in the sewage must be accounted for by some other reactions.

Intermittent Action of Filters.

That there is a need for intermittency in dosing a filter is shown by the following considerations. Particles of organic matter concentrated at the interface of the jelly and sewage are liquefied by enzymes. They are then taken into the living cells at a rate dependent upon the utilization of these substances inside the cell. Since the predominant reaction in a filter are oxidations, this utilization depends largely upon the amount of oxygen available for this purpose. Thus the absolute amount of oxygen available, as well as the oxidation potential, regulates the oxidation of substances in the cell. This, in turn, regulates the rate of entry of organic molecules into the cells. Finally, dependent on this rate, is the rate of concentration at the interface. Hence the more oxygen available, the more colloids can be concentrated at the interface, dissolved, diffused into the cell and finally oxidized.

Since one liter of saturated water at 20° C. contains about eight milligrams of dissolved oxygen, and one liter of air contains 250 milligrams of oxygen, it can be seen that a given quantity of air in contact with the bacterial jelly contains thirty-one times as much available oxygen as the same quantity of saturated water or sewage. Furthermore, as it is being dissolved or adsorbed by the jelly, the diffusion of more oxygen molecules to the jelly is far more rapid through air than through sewage, since diffusion rates depend largely upon the viscosity of the media. If a continuous flow of sewage is allowed to trickle over the jelly, the necessary oxygen must come from that dissolved in the sewage. The intermittent sand filter is a very good illustration of the fact that there is not enough oxygen in solution in sewage to permit purification. We have secured some data which point to the same conclusion.

On the other hand, when intermittent dosing is employed, air is drawn into the bed to replace the receding sewage. With the far greater amount of oxygen thus introduced, and the higher rate of diffusion to the jelly, the necessary oxygen is rapidly absorbed. The activated sludge process illustrates the fact that as more oxygen is furnished the amount of nitrification increases.

Theoretical Discussion of the Progress of Purification.

An insight into the probable progress of purification at different depths of the filter can be gained by a brief consideration of several related phenomena. One of these is the law of mass action, or law of molecular concentration, which states that the rate of a reaction increases with increasing concentrations of reacting substances (*see* Chapter I). With this established law in mind, it is not unreasonable

to expect greater removal of ammonia and colloids by the upper part of a filter where they are more concentrated than at any other point in the bed. As the sewage trickles through the filter, these substances are removed, the concentration is lowered and hence the reactivity or rate of removal should be reduced. We would predict that an equilibrium should be reached at some depth beyond which the degree of purification is increased only very slightly, if at all. Furthermore, the purification of sewage in a filter is due to biochemical reactions which, in common with most expressions dealing with vital activity, cannot be considered as simple linear functions of time. The commonest example is the work of Chick,[31] which indicates that in disinfection the death rate of bacteria is proportional to the number of living cells at any given time. With certain limitations, the process follows a logarithmic expression similar to that for adsorption, a first-order chemical reaction, rate of solution, etc. In a later section are presented biochemical oxygen demand data which also show that processes dependent upon vital activity do not vary directly with time.

The removal of ammonia by activated sludge further illustrates the manner in which reaction rate is affected by concentration. Bartow and Mohlman [32] found that fifty-two per cent of the ammonia was removed in the first hour of aëration and only about eighteen per cent in the second hour. The rate gradually dropped off until, during the fifth hour of aëration, no more ammonia was removed. If we apply these data to the sprinkling filter, we can use depth of bed instead of time of contact with the growth, since the distance covered by the liquid in trickling down through the bed is proportional to time. Because of the analogy between the two processes, we might well expect a greater removal of ammonia in the upper part of a filter bed where the concentration is at a maximum. This has been found to be true, and curves showing ammonia removal in a filter bed are very similar to those showing ammonia removal by activated sludge.

In virtue, then, of theoretical reasoning on the basis of the law of mass action, and of practical evidences of the truth of this law in similar processes involving living cells, we do not believe that the current practice of assuming an equal degree of purification by each foot of filter depth is justifiable. The data secured in this investigation confirms our belief that the upper portion of a filter is far more effective than the lower portion.

Summary of Theoretical Discussion.

Our conception of the mechanism of the purification process may be summed up briefly:

[31] Chick, H., "An Investigation of the Laws of Disinfection," *J. Hygiene*, **8**, 92 (1908).

[32] Bartow, E., Mohlman, F. W., "Purification of Sewage by Aëration in the Presence of Activated Sludge," *J. Ind. Eng. Chem.* **7**, 318 (1915); *ibid.*, **8**, 15 (1916).

1. Colloidal and soluble substances which lower the surface tension of water concentrate at the jelly-sewage interface.

2. These adsorbed substances are attacked by enzymes, bacteria and higher forms of animal life and the ammonia thus liberated is subsequently oxidized by bacterial or chemical means.

3. A flocculent, humus-like residue of large surface area accumulates in the filter until the semi-annual unloadings.

4. Since sufficient oxygen for the oxidation reactions cannot be obtained from that dissolved in the sewage, it is necessary to operate the beds intermittently to cause atmospheric oxygen to come in contact with the bacterial film.

5. The analogy between the purification process and several other biological phenomena, together with a consideration of the law of mass action and the adsorption formula leads to the conclusion that the bulk of the purification is effected in the upper part of the filter where the sewage is most concentrated.

Relation of Depth to Degree of Purification. Summary of Previous Work.

A survey of the previous work [33] on this question of the progress of purification at different levels in a filter makes it apparent that when filters of different depths are dosed at the same rate per unit of surface area, and the same volume of sewage trickles through the different filters, the rate of purification is greatest where the concentration of removable impurities is greatest, i.e., in the upper few feet of the filter. In experiments conducted on the basis of equal dosage per cubic yard, the results do not agree with those obtained on the basis of equal dosage per square yard. The reason for this will be apparent when the conditions are scrutinized more closely. If two filters of equal area and of four and eight feet depth, respectively, are dosed with equal amounts of sewage per cubic yard, then the deep filter will receive twice the total amount of sewage received by the four foot filter. Hence twice the amount of sewage will trickle over the first two feet, for example, of the deep filter as compared to the first two feet of the shallow filter. Naturally, being loaded to twice the extent, the first two feet of the deep filter do not

[33] *British Royal Commission on Sewage Disposal*—Fifth Report (1908), p. 70; Metcalf, L., and Eddy, H. P., "American Sewerage Practice," Vol. **III,** 561 (1916); Greeley, S. A., "Some conclusions drawn from a recent survey of sewage treatment plants," *J. West. Soc. Eng.*, **27,** 250 (1922); *Report of the Baltimore Sewerage Commission* (1911), p. 59; *Report of the Bureau of Surveys, Philadelphia,* 1911, 7; Clark, H. W., *Mass. State Dept. of Health Rept.*, 1915, p. 393; *ibid.*, 1919, p. 108; Fuller, C. W., "Economics of sewage filters," *Am. Soc. Mun. Imp.* **21,** 113 (1914); "Discussion of the economic depth of trickling filters," *J. Boston Soc. Civ. Eng.* **2,** 63 (1915); Eddy, H. P., "The economic depth of trickling filters," *J. Boston Soc. Civ. Eng.* **2,** 49, 191 (1915); Smith, R. O., "Annual Report Sewage Substation for year ending June 30, 1922," *Rept. Dept. Entomology, New Jersey Agric. Expt. Sta.*, 1923, p. 487; Campbell, F. L., Rudolfs, W., "Studies of the biology of sewage disposal," *Repts. Sewage Substation, New Jersey Agric. Exp. Sta., Bull.* **390,** 18 (1923).

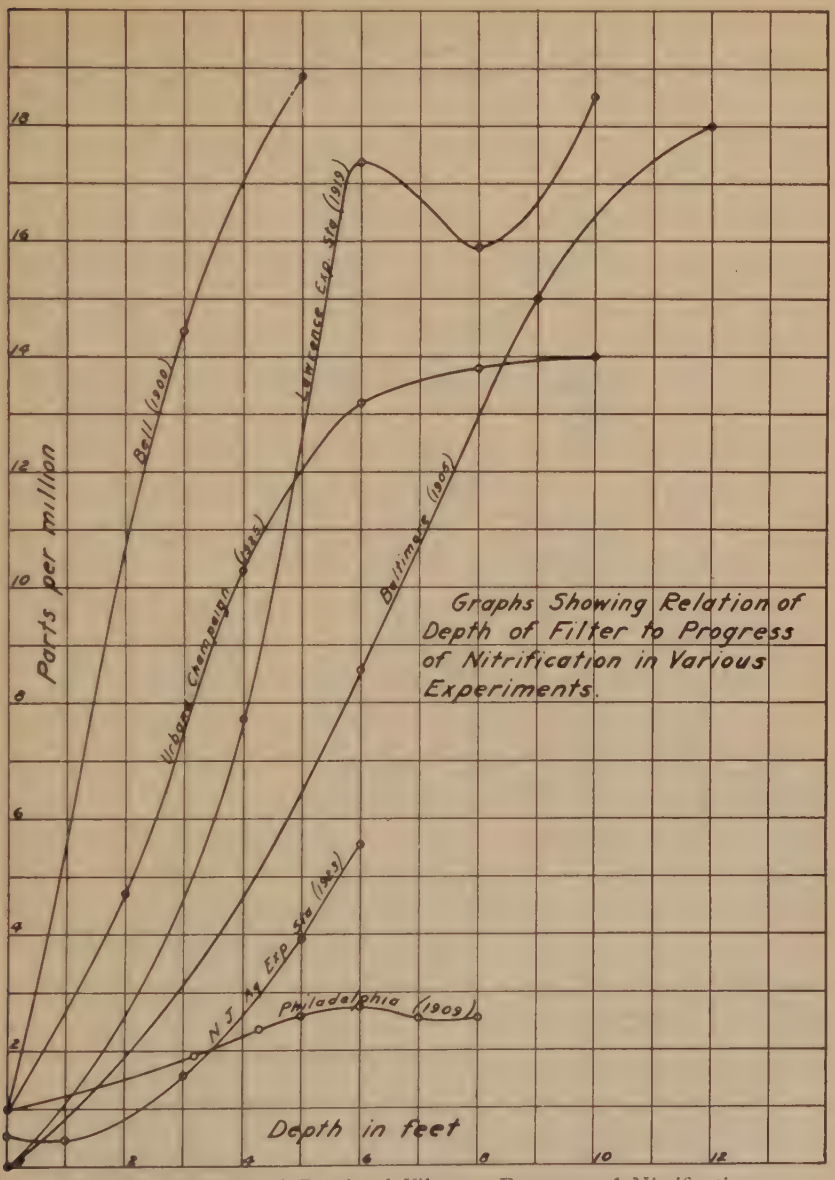


FIG. 49.—Relation of Depth of Filter to Progress of Nitrification.

purify sewage as well as the less heavily dosed two feet of the shallow filter, and the value of the upper portion of the filter is obscured.

If the progress of purification is to be studied in relation to the depth of the filter, then it is obvious that fair samples taken at

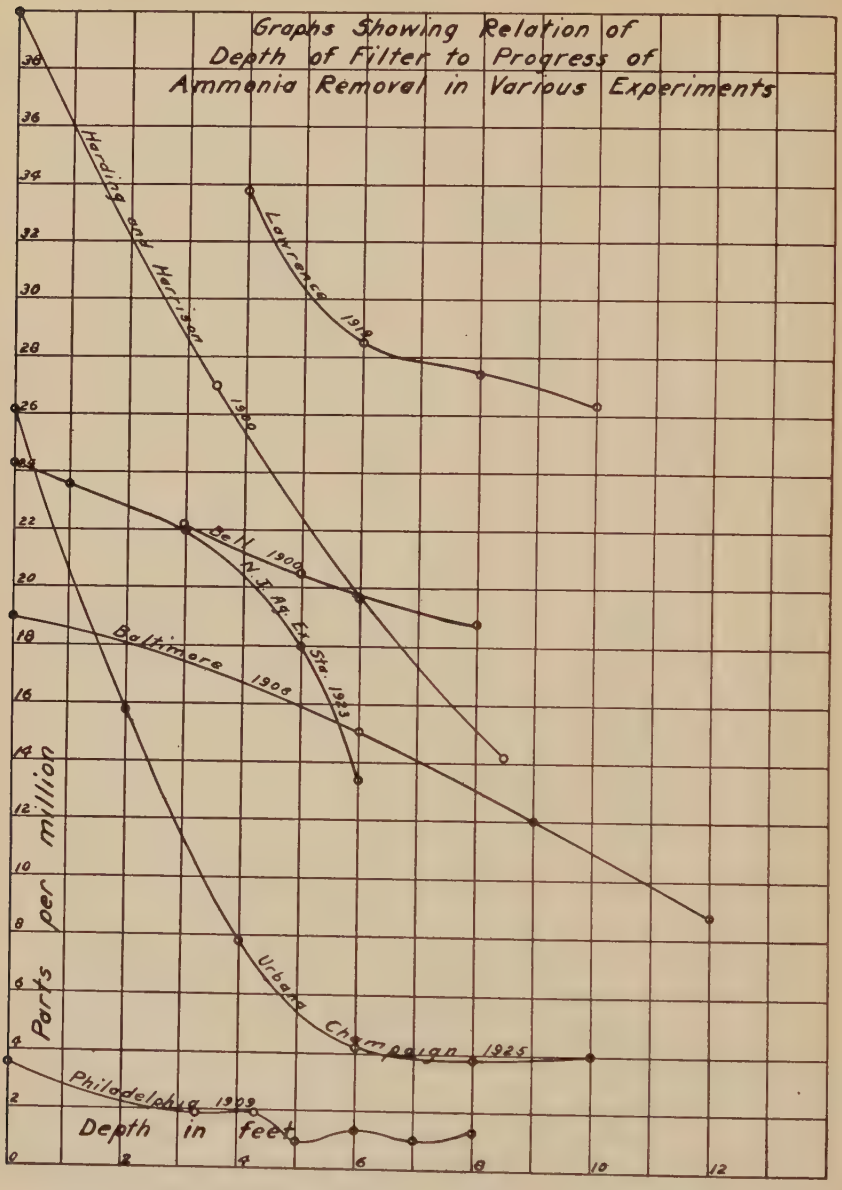


FIG. 50.—Relation of Depth of Filter to Progress of Ammonia Removal.

different depths would furnish the data necessary to judge the degree of purification attained at the sampling depth. Because of certain inherent difficulties in such sampling procedures, different filters of

TABLE 41.—*Organic Matter at Different Depths of Filter and at Different Rates of Dosing.*

Rate of Dosing	Turbidity	Oxygen consumed	NH_3	Org. N.	Conversion NH_3 to NO_3 in percent of original NH_3	Stability
million gallon/ acre/day	ppm.	ppm.	ppm.	ppm.		percent
			2-foot level			
1.5	65	41	52	39	25	42
2.1	67	39.0	40	55	18	57
3.25	55	32	43	37	13	49
			4-foot level			
1.5	79	53	82	75	43	90+
2.1	79	50	84	56	45	90+
3.25	72	39	63	50	22	81
			6-foot level			
1.5	81	57	94	79	55	90+
2.1	79	57	92	63	50	90+
3.25	79	44	74	55	29	89
			8-foot level			
1.5	84	62	92	68	46	90+
2.1	82	52	91	66	45	90+
3.25	77	48	75	38	31	89
			10-foot level			
1.5	85	60	89	61	55	90+
2.1	79	50	85	53	50	90+
3.25	79	50	74	42	29	89

various depths may be used. But it is necessary to have the sewage applied at the same rate per unit of surface area to each filter, just as is done in the case of the large filter with sampling devices at different levels. In that way, all variable conditions are eliminated, with the exception of those relating to the depth of bed through which the sewage trickles, and the progress of the purification process can then be traced.

Figures 49 and 50 show graphic summaries of previous results obtained in a number of different experiments. For the sake of comparison, our results are also included.

Following the review of earlier work on sprinkling filter depth Strickhouser carried on a series of tests on the quality of the effluent from different levels of a ten-foot filter. The investigation extended over a year's time and included observations made at different rates up to a dosage at which extensive ponding occurred. The results are summarized in Table 41 and in Figures 49 and 50. They agree with the previous work in indicating a marked falling off in efficiency of the lower levels. The depth at which efficiency begins to drop off will depend on the size of the stone and on the strength of the sewage. In experiments so far conducted it does not seem to depend upon the rate of dosing to any marked extent.

Ventilation.

There are some differences of opinion regarding the supply of oxygen needed for the stabilization of organic matter which takes place during its passage through the trickling filter. Standard text books [34] point out that the supply of oxygen is obtained by the downward movement of air through the filter. According to a report [35] regarding the trickling filters at Austin, Minnesota, where a specially constructed underdrain is used, there was an *upward* velocity of about sixty feet per minute in the underdrains as determined with an anemometer.

In order to supply sufficient oxygen, filters have been constructed with rather elaborate and expensive bottoms and underdrain systems. Care has been taken in the construction of filters to maintain a depth usually less than ten feet and to avoid the use of fine rock, because of the danger of clogging of the filter as well as the possibility of depleting the oxygen supply.

In view of studies on the rate of solution of gases [36] and the general knowledge regarding the tendency of gases to maintain uniform composition by rapid diffusion, it seemed unlikely that the rate of biological oxidation in trickling filters was sufficient to seriously deplete the oxygen supply. The report of Wagenhals [37] on sewage treatment in the United States does not indicate that different ventilating systems aid materially in sewage purification.

[34] Fuller and McClintock, *Solving Sewage Problems,* McGraw-Hill; Babbitt, *Sewerage and Sewage Treatment,* Wiley; Metcalf and Eddy, *Sewerage and Sewage Disposal,* McGraw-Hill.

[35] What Cheer Clay Products Company, What Cheer, Iowa, *Bulletin—The Rawn Underdrain Tile.*

[36] *State Water Survey, Urbana, Ill., Bulletin 19,* "Solubility and Rate of Solution of Gases."

[37] Wagenhals, H. H., "Sewage Treatment in the United States," *U. S. Pub. Health Bull.* 132.

A recent investigation by Buswell and Elder [38] reports analytical data on the composition of air in filters. No significant depletion of oxygen was noted even in a filter constructed with underdrains which were inadequate to drain the water properly.

[38] Paper, *12th Ann. Mt. New Jersey Sewage Wks. Assoc.*

Chapter XXI.

Removal of Colloids from Sewage by Activated Sludge.*

Development of the Activated Sludge Process.

This process of sewage treatment, already briefly described in Chapter XV, has been the subject of extensive research during the last fifteen years.

For the sake of completeness an historical sketch [1] will be quoted here:

> The earliest attempts to oxidize sewage by aëration were made by Dupré and Dibdin [2] on the sewage of London, and by Dr. Drown [3] on the sewage of Lawrence, Massachusetts. They found that oxidation accomplished in this way was a very slow process, and accordingly not at all practicable.
>
> In 1892 Mason and Hine [4] conducted experiments on the oxidation of sewage by means of aëration. They concluded that air had but little oxidizing effect on sewage. In 1894 Waring [5] attempted to apply air on a working scale at Newport, R. I., but his project was unsuccessful.
>
> In 1897 Fowler [6] aërated the effluent from the chemical precipitation tanks at Manchester, England, but without accomplishing any considerable degree of purification. In 1911 aëration was again attempted. Black and Phelps [7] studied the possibility of aërating the sewage of New York City. They used tanks filled with inclined wooden gratings for varying periods up to twenty-four hours. The oxidation was so light that determinations of nitrogen showed prac-

* Since this chapter was written an extensive treatise ("The Activated Sludge Process" by Arthur J. Martin, Macdonald and Evans, London) has appeared on this subject.

[1] Mohlman, F. W., Bartow, E., "The activated sludge method of sewage treatment," *Ill. State Water Survey*, Bull. **14**, 77.

[2] Dupré, A., Dibdin, W. J., *Rept. to Royal Comm. on Met. Sewage Disposal*, **2**, 1884.

[3] Clark, H. W., and Adams, G. O., "Sewage treatment by aëration and contact in tanks containing layers of slate," *Eng. Record*, **69**, 158 (1914).

[4] Mason, W. P., and Hine, S. K., "Note on the direct oxidation of organic matter in water," *J. Am. Chem. Soc.*, **14**, 233-8 (1892).

[5] Rafter, G. W., and Baker, M. N., *Sewage Disposal in the United States*, p. 535, London, 1894.

[6] Fowler, G. J., *Annual Report of the Rivers Department of the Corporation of Manchester*, 1897.

[7] Black, W. M., and Phelps, E. B., *Report on location of sewer outlets and discharge of sewage into New York Harbor*, pp. 64-78 (1911).

tically no purification, although some measure of improvement was indicated by the incubation tests. Black and Phelps recommended the process for a large-scale installation but it was not adopted.

Clark, Gage and Adams[8] had tried aëration of sewage at the Lawrence Experimental Station, but had been unable to obtain satisfactory results until 1912. In that year, however, they were able to nitrify sewage successfully by aëration for twenty-four hours in a tank containing vertical slabs of slate placed about one inch apart, and covered with a zoogleal mass of colloidal matter deposited from the sewage. They submitted the effluent to further treatment for they did not claim that the aëration would entirely obviate filtration.

Gilbert J. Fowler,[9] of Manchester, England, had tried aëration with some modification on English sewages, but had obtained only indifferent results. Upon his return to England after a visit to Lawrence in 1912, he suggested work on aëration to Ardern and Lockett, resident chemist and assistant chemist, respectively, at the Davyhulme Sewage Works of Manchester. On April 3, 1914, they reported[10] the remarkable results which they had obtained in their preliminary investigations.

In their first experiment, Arden and Lockett aërated samples of Manchester sewage in gallon bottles until complete nitrification was accomplished. The aëration was affected by drawing air through the sewage with an ordinary filter pump. Aëration for about five weeks was required to obtain complete nitrification. The clear oxidized liquid was then removed by decantation, raw sewage added to the deposited sludge, and aëration continued until the sewage was again completely nitrified in six to nine hours.

The sludge which induced such active nitrification was called "activated sludge" by Ardern and Lockett.

In August, 1914, Edward Bartow[11] saw the work in progress at Manchester, and upon his return to this country, suggested that experiments with activated sludge be started at the University of Illinois.

Experiments on the purification of sewage by aëration in the presence of activated sludge were begun at the laboratories of the Illinois State Water Survey in November, 1914, and have been continued to the present date. The first series carried out by Bartow and Mohlman included experiments in three-gallon bottles, a small tank with glass sides five feet deep, and later concrete tanks of ten square feet area,

[8] Clark, H. W., and Gage, S. DeM., "The purification of sewage," *Mass. State Board of Health, 45th Annual Report* (1913), pp. 228-304.

[9] *Op. cit.*

[10] Ardern, E., and Lockett, W. T., "Experiments on the oxidation of sewage without the aid of filters," *J. Soc. Chem. Ind.*, **33**, 523-539, 1122-4 (1914).

[11] Bartow, E., and Mohlman, F. W., "Purification of sewage by aëration in the presence of activated sludge, I and II," *J. Ind. Eng. Chem.* **7**, 318-23 (1915); **8**, 15-16 (1916); *Eng. News*, **73**, 647-8 (1915); **74**, 1096-7 (1915); *Eng. Contr.*, **43**, 310 (1915); **44**, 433-4 (1915); *Eng. Record*, **71**, 421-2 (1915).

and eight feet five inches deep. This series demonstrated the effect of activated sludge on the rate of nitrification, the superiority of filtros plates as air diffusers over wood diffusers, and furnished data on the ratio of diffuser area to tank area. These experiments are completely reported in Illinois State Water Survey Bulletin 13.

During this series of experiments such problems arose as the required area for air diffusion, the nitrogen cycle, the time of aëration, the fertilizing value of the sludge, the required sludge for purification. The fill and draw method proved inadequate and attention was given to the construction of a new plant.

In the summer and fall of 1916, the septic tank designed by Professor A. N. Talbot in 1897 for the city of Champaign was reconstructed into a continuous-flow plant where the second series of experiments on the activated sludge process was conducted. A full description of the plant, results and conclusions are given in an article by Professor Bartow.[12]

Recent Progress.

In the meantime a relatively enormous amount of experimental work has been in progress throughout the world. Porter's bibliography [13] lists over eighty experimental plants and seventeen municipal activated sludge plants completed or in process of construction at that date together with some eight hundred articles.

In this country a most extensive series of experiments has been carried on at Milwaukee, Wisconsin, leading to the design and construction of an activated sludge disposal plant for the entire city of Milwaukee.[14] A plant has been in operation in Houston, Texas, since 1917. A report on operating results will be found in *Eng. News-Record,* **85,** 1128. San Marcos, Texas, with a sewage flow of 150,000 gallons per day, is believed to be the first town in the United States to use activated sludge treatment for its entire sewage.

Considerable progress in the treatment of trade wastes by the activated sludge process has been made by the Sanitary District of Chicago. The British experiments have been along somewhat different lines from the American, and will be described under special headings.

[12] Bartow, E., "Purification of sewage by aëration in the presence of activated sludge, III," *J. Ind. Eng. Chem.,* **9,** 845-50.

[13] *The Activated Sludge Process of Sewage Treatment, a bibliography of the subject,* by J. Edward Porter, General Filtration Co., Jan., 1921.

[14] Metcalf and Eddy, *Sewerage and Sewage Disposal,* Chapter XIV.

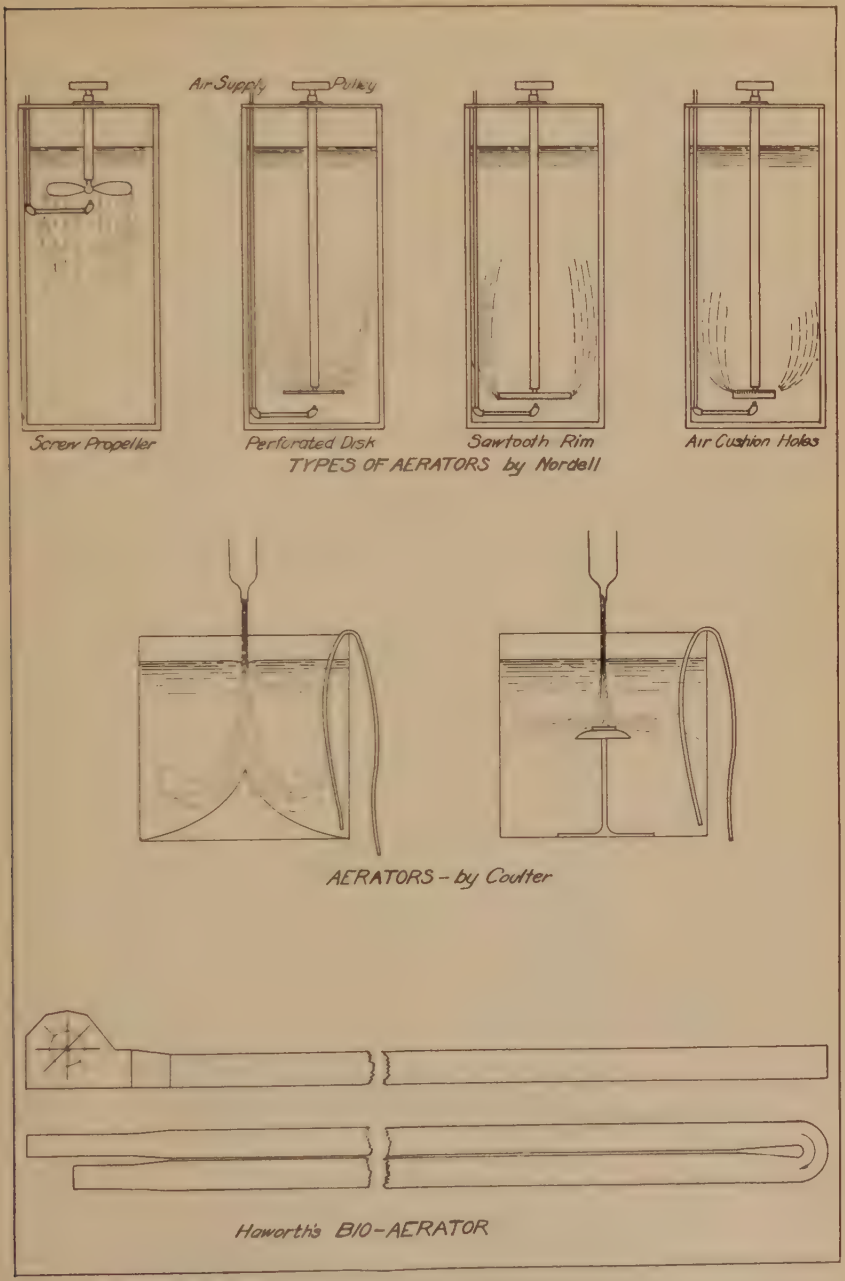


Fig. 51a.—Types of Aërators.

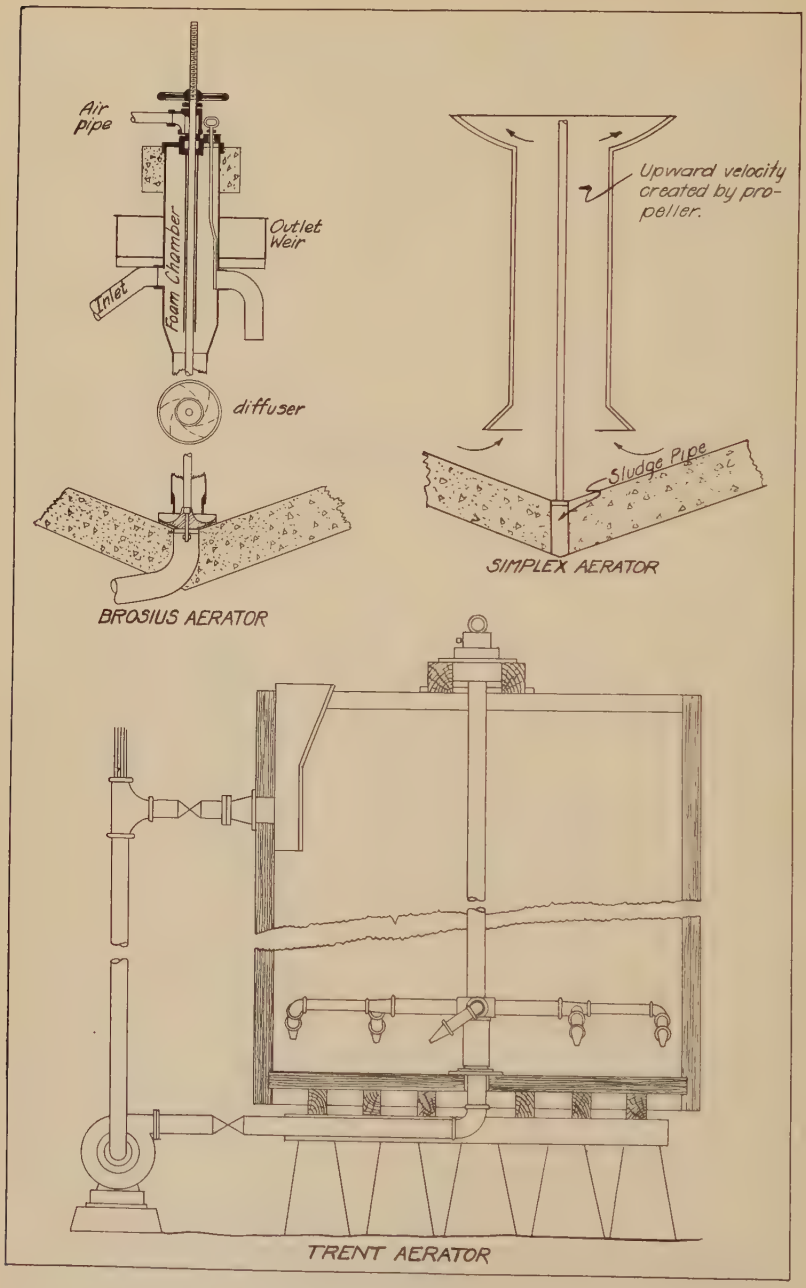


FIG. 51b.—Types of Aërators.

Mechanical Aëraters.

One of the most extensively investigated problems is that of reducing the amount of power required to supply the air necessary for maintenance of the proper operation of the activated sludge process. Unless the cost of operation can be very materially reduced or considerable return realized on the sludge the process will be of very limited application.

We have found in going through the technical and patent literature some thirty articles or patents describing either methods of introducing air into sewage other than by blowing through porous tile, or methods for increasing the period of contact and efficiency of air when once blown into the sewage.

A few of the methods which have been employed with more or less success for the introduction of air into sewage other than by blowing through porous plates will be discussed. Figures 51a and 51b show illustrations of nine such methods.

Coulter [15] describes experiments in which he forced water under considerable pressure through a nozzle, allowing it to strike upon the surface of the liquid in the tank. The force of the stream carried a considerable amount of air down into the liquid. In fact, by using a large diameter pipe directly beneath the point where the stream struck the liquid in the tank, thereby producing a sort of suction pump, it was found possible to carry air bubbles several feet beneath the surface of the liquid. This method has not to our knowledge been employed on a large scale in purifying sewage.

A second method which was employed by Brosius [16] and Trent [17] independently, produces a mixture of air and liquid by drawing or forcing the liquid rapidly down a vertical pipe at such a rate that air is mechanically carried down with the water. In the Trent apparatus a series of small pipes inside the larger vertical downtake pipe facilitated the introduction of air. In neither of these machines were the conditions produced satisfactory for the maintenance of activated sludge.

A third method for introducing air, and one which has been frequently attempted, is that of surface aëration. Haworth [18] appears to have successfully operated an activated sludge plant by surface aëra-

[15] Coulter, W. S., "Air diffusion in activated sludge," *Eng. News-Record*, **78**, 255.

[16] Brosius, A. M., "Activated sludge novelties at Hermosa Beach, Cal.," *Eng. News-Record*, **76**, 890.

[17] Orbison, R. V., "Test of Trent activated sludge devices at Pasadena," *Eng. News-Record*, **85**, 1287.

[18] Haworth, John, *Report on sewage disposal at Sheffield, England*, July, 1921.

tion at Sheffield, England. He causes the sewage and activated sludge to circulate through long channels. These channels are approximately four feet wide and four feet deep. The rate of flow is just sufficient to maintain the sludge in suspension and amounts to one and one-half feet per second. Housings cover paddle wheels which force the liquid along the channels. This plant has a capacity of 500,000 gallons of sewage per day and has been in successful operation for six years. The capacity is equivalent to 1.3 million gallons per acre per day and the power equals 50 horsepower per million gallons.

One point which should be mentioned in connection with the success of this particular experiment is that there is a considerable amount of iron or pickle liquor waste in the raw sewage. It will be remembered that Mumford in describing her bacterium M7 called attention to the importance of iron.

Another mechanical process which seems to have found practical application is the "Simplex," [19] installed by the Ames Crosta Sanitary Engineering Company, Ltd., at Bury, England, and elsewhere. The tank is arranged with a conical bottom, and a central tube coned at the lower end is fixed a few inches from the bottom of the tank, the top portion terminating in a dish, the outer edge of which is raised about half an inch above the top water level. Inside the dish a revolving cone with suitably formed vanes is suspended by means of a vertical shaft running on ball bearings rotated by shafting and bevel wheels.

Of the various methods of economizing on air we should like to call attention to the intermittent aëration proposed by Burn.[20] This author suggests cutting off the air during the peak of the power load. If the peak does not last more than three or four hours, satisfactory results might be obtained.

The writer recently saw an interesting combination of mechanical agitation and compressed air aëration in Birmingham, England. The action of the paddles was less violent than some other types, having less tendency to break up the flocs. Their mechanical efficiency was also said to be better than some designs.

Automatic Sludge Return.

A number of attempts have been made to build activated sludge tanks so that settled sludge could be returned automatically or without pumping to the aëration chamber. Among the previous investi-

[19] "Simplex" sewage plants, *Surveyor*, **61**, 327 (1922); *Eng. Contr.*, **57**, 527.
[20] Burn, G. A. H., "Intermittent aëration in activated sludge process," *Can. Eng.*, **40**, No. 24, 1.

gators who have designed such apparatus might be mentioned the following:

Frank [21] describes a tank with a central aërating chamber, and two elevated side chambers with a V cross-section, the aëration taking place in the central chamber from which the aërated sewage overflows into the side chambers where sedimentation takes place. The bottoms of these chambers are open so that the settled sludge drops back into the aërating chamber.

Martin [22] describes a cylindrical tank divided into segments. A radial trough is provided for sedimentation, from the bottom of which the settled sludge may be returned to the aërating segment. Hammond's tank [23] had an upper and lower chamber, the lower chamber being used for aëration and the upper chamber for sedimentation. The settled sludge could be returned by gravity. Moore [24] describes a two-chamber tank with means for discharging the thickened sludge from the lower portion of the second tank directly back to the first. Adams' sedimentation tank [25] had an apron roof in which sedimentation took place in the upper portion of the tank on the apron, the settled sludge slipping through a slot into the lower portion of the chamber.

Other means for accomplishing these results have no doubt been employed. The above are mentioned simply as examples of progress in this direction.

Theory of the Activated Sludge Process.

In reviewing the opinions of experimenters with regard to the theory underlying the activated sludge process of sewage disposal one soon comes to the conclusion that two main lines of action are held responsible for the results obtained. That the mechanism of the reaction is sometimes described as that of adsorption of the colloidally dispersed matter by sludge already present in the sewage is evident from the following statement quoted from well known authorities: [26]

"The sludge embodied in sewage and consisting of suspended organic solids, including those of a colloidal nature when agitated with air for

[21] Frank, L. C., "Process of purifying sewage or other wastes," *J. Soc. Chem. Ind.*, **34**, 680.

[22] Martin, E. B., "Method of and apparatus for the treatment and purification of sewage," *J. Soc. Chem. Ind.*, **36**, 160.

[23] Hammond, G. T., "The aëration and activation of sewage," *Surveyor*, **49**, 255-7.

[24] Moore, G., "Sewage Treatment," *J. Soc. Chem. Ind.*, **37**, 603 A.

[25] Adams, S. H., "Separation of sludge and scum from sewage and other liquids," *J. Soc. Chem. Ind.*, **39**, 581.

[26] Hatton, T. Chalkley, and Copeland, W. R., "Activated sludge defined," *Eng. News*, **75**, 503.

a sufficient period, assumes a flocculent appearance very similar to small pieces of sponge. Aërobic and facultative aërobic bacteria gather in these flocculi in immense numbers, some having been strained from the sewage and others developed by natural growth." In other words, the usual suspended particles in sewage grow by the accretion of material colloidally dispersed, thus producing activated sludge.

Other writers refer to the "scrubbing action" of suspended particles, and compare the action of activated sludge to that of coagulated alum.[27] The process is often referred to as one of oxidation, assuming that oxidation is a principal step in the purification of sewage. Another definition states that activated sludge must be of "a character to absorb colloidal matter," and another author [28] refers to the "clotting" of the colloids in the sewage. Such expressions seem to indicate what might be called a colloidal or mechanical theory for the mechanism of the action of activated sludge, similar in many respects to the Hampton doctrine of the action of sewage filters.

Another theory, which in reality seems to have been the first to be proposed, is what might be called the biological theory and resembles Dunbar's theory of sewage filters. Those emphasizing this viewpoint of the action of activated sludge call attention [29] to the analogy between the action of slate beds, contact beds, and sprinkling filters and the action of activated sludge. The sludge is referred to by these writers, not as a clotted, agglomerated or coagulated sludge produced by the mechanical growth of suspended particles in the sludge, but as biological growths arising from the germination and propagation of microorganisms whose "spores" are always present in sewage. The term "cultivated sludge" used by one author,[30] and "animate energy" used by another [31] contrast as strongly as any with the term "coagulated" or "agglomerated" sludge, used by those favoring the colloidal theory.

If one examines particles of activated sludge under the microscope he is immediately impressed with the fact that there is practically no absorbed, precipitated or coagulated amorphous matter in these sludge particles, but that they are composed entirely of active, growing microscopic organisms of varieties ranging from true bacteria up through the giant bacteria, with occasional molds and yeasts, and also a variety

[27] Eddy, H. P., "Lights and shadows of the activated sludge process for the treatment of sewage and industrial wastes," *J. Western Soc. Eng.*, **26**, 259.

[28] Fowler, G. J., "The activated sludge process of sewage purification," *J. Inst. San. Eng.*, **20**, 29-38.

[29] Clark, H. W., and Gage, S. DeM., *44th Annual Report State Board Health, Mass.*, 1912, 275.

[30] Jones, Jones and Atwood, *British Patent No. 729.*

[31] Harris, *51st Ann. Congress Roy. San. Assoc. Scotland.*

of free swimming and attached protozoa.[32] These communities of microörganisms must obtain food and this food must be supplied from the colloidal and dissolved matter and salts in the sewage. From what we know of the metabolism of microörganisms it is probable that the unicellular forms absorb through their membrane such soluble forms of organic matter as are able to pass through this membrane, and that they also secrete enzymes which are capable of peptizing or liquefying colloidal particles too large to be directly absorbed. Protozoa, on the other hand, can easily be seen to approach and ingest visible particles of organic matter. This biological theory of the action of activated sludge may be summarized and emphasized by proposing what seems to be a rather striking analogy, namely, that the purification of sewage effected by microscopic communities appearing as flocs is entirely similar to that of disposal of garbage by feeding it to hogs. It does not seem probable that adsorption of colloids or mechanical precipitation play any greater part in the metabolism of microörganisms that they do in the digestion of the larger animals. One serious objection to the colloidal theory of coagulation is that the colloidal particles in sewage and the activated sludge particles are, so far as we are able to determine, both negatively charged. Since adsorption of colloids is most effective between oppositely charged particles it should not be applied to the conditions of the activated sludge particles without reservation. Furthermore, adsorption is an almost instantaneous action, while considerable time is required for the activated sludge reaction.

If the action is largely colloidal and mechanical, then we shall need to study particularly the colloid chemistry of the sewage. If, on the other hand, it is biological, we should study the biology of the sludge so that we may obtain complete knowledge of the desirable and undesirable members of these microbial communities upon which we are to rely for the purification of sewage.

The biological theory suggests a somewhat different notion of the importance of oxidation in sewage purification than that ordinarily expressed. When garbage is disposed of by feeding to hogs, only as much oxidation takes place as is required to furnish energy for the life processes of the hogs. Final oxidation does not take place until the pork chops are eaten and burned up in the body to furnish human energy. If the analogy of this process to sewage disposal is admitted, oxidation appears as an incidental reaction. Clark,[33] in 1912, called

[32] Purdy, W. C., "Treatment of strawboard wastes," *U. S. Pub. Health Service Bull.*, 97, 45.

[33] *Op. cit.*, p. 292.

attention to this viewpoint in the following manner: "In experiments upon aëration of sewage tried during the past twenty-five years by various investigators, as described by Drown, Dupré and Dibdin, Mason and Hine, Black and Phelps, etc., the chief object of each study has been to learn the oxidation changes induced by such treatment. The collection of suspended and colloidal matters, as here described, is an entirely new feature of aëration work."

To quote Harris further, activated sludge is a term the too literal interpretation of which might be taken as suggesting an association of the process with the solid matter or crude sludge of raw sewage. No such association exists.

Analysis of Steps in the Process. The Action of Air.

A more detailed analysis of the steps in the process is given by Buswell.[34] When air is blown into the aëration chamber of an activated-sludge plant it does three things: (*1*) It maintains the sludge in suspension. (*2*) It maintains aërobic conditions. (*3*) It stirs up the mixture, allowing fresh liquor to come into contact with the sludge. We are not able to tell, therefore, which one of these three factors determines the critical minimum air requirement. In mechanical aëration processes we also have the same three factors determining the critical velocity, namely, 1½ feet per second, which it is found necessary to maintain in the circulating chamber. The importance of maintaining the sludge in suspension is due to the fact that otherwise the sludge could not come into contact with the liquid and also to the fact that if the sludge is allowed to stand it very soon begins to putrefy and redisperse and the work done in building it up is lost. The relative importance of aërobic conditions and stirring cannot be balanced by means of any present data. Accordingly we have undertaken an investigation to determine the minimum air requirement of the microbial growths composing the sludge. To do this it was necessary to hold one at least of the three variables constant, thereby allowing us to balance the other two.

We decided upon adopting some mechanical means for maintaining the sludge in suspension. Various materials, such as strings, copper, zinc and iron gauze, were used to support the sludge while arrangements were made for circulating and aërating the sewage. As a result of several such experiments we were able to produce an abundant growth of sludge, very good clarification and a substantial purification

[34] *Eng. News-Record*, **90**, 835 (1923).

of sewage in from three to six hours when using as low as 0.002 cu. ft. of air per gallon.

The Importance of Stirring. If we consider the various steps which must take place in the activated-sludge process it will be apparent why stirring is of such great importance. There are apparently four important points involved in this process, each of which are represented in Figure 52 as follows: (I) The water surface, by a straight line; (II) an activated-sludge floc, by a rough oval; (III) a colloidal particle of organic matter, by a large dot; (IV) a dissolved molecule of organic matter, by a small dot.

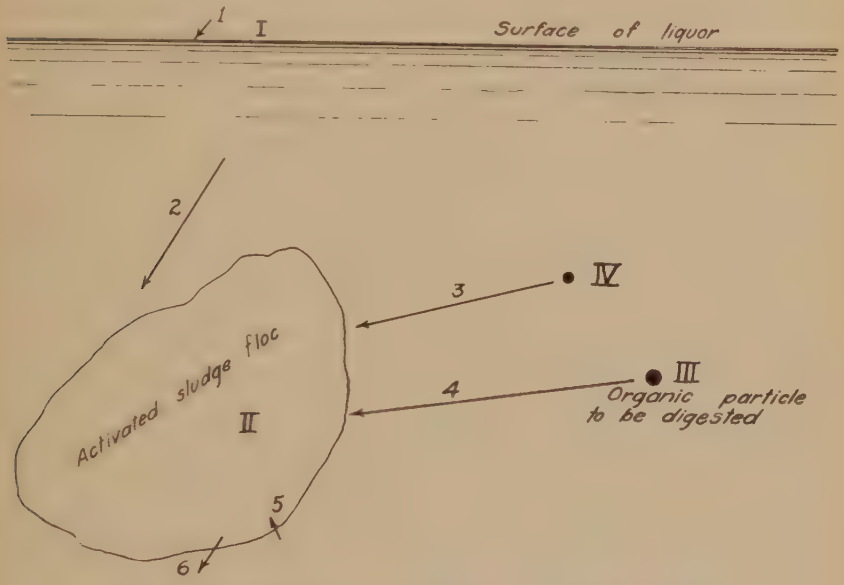


FIG. 52.—Six Steps in the Formation of Activated Sludge.

The Six Steps of the Process. We shall discuss the process in terms of six reactions:

(1) The air must saturate the liquor or water immediately below the surface of contact. Langmuir has shown that enough molecules strike such a surface to saturate it in an infinitesimally short time, giving a thin layer of water saturated with oxygen immediately in contact with the air surface.

(2) This oxygen must then diffuse to the activated-sludge particles. This is an exceedingly slow process as was pointed out more than

twenty years ago by Noyes and Whitney and later emphasized by Phelps.

(3) The dissolved molecular organic matter must diffuse to the activated-sludge particles. This also being a diffusion process is slow.

(4) The colloidal particles must get to the activated-sludge floc somehow or other. The actual change of position of colloidal particles is practically zero.

(5) The organic material and the oxygen must be taken up and worked over by the organisms of the sludge floc. As far as we are able to tell this is a comparatively rapid process.

(6) The by-products of the biological growth must diffuse away from the sludge floc; otherwise they will accumulate and poison it.

Of the six steps which must take place, all except (1) and (5) are comparatively slow. The only way that we can speed up the other four steps in this process is by stirring. Stirring will sweep away the saturated film from the air surface and bring it down in contact with the activated-sludge particles. It will move the dissolved and colloidal organic matter about so that they come in contact with the floc and will sweep away the metabolic products of the sludge organisms. In view of this analysis it does not seem so strange that stirring should prove to be more important than air in the carrying out of this process. Stirring by means of blowing air through sewage is, however, a rather inefficient process. We do not get as much stirring for the power input as we would if the power were applied in some other way. When air is blown into sewage, the activated-sludge floc, air bubbles and liquid are all driven in the same direction. The most efficient process would be one in which the air surface and flocs would be held stationary while the liquor is caused to flow past them.

Bio-Precipitation by Sewage Organisms.

Various terms more descriptive of the process have been suggested to supersede the earlier one "activated sludge." Of these "bio-aëration" seems to have much to commend it. Shive and Buswell [35] call attention to the fact that both dissolved and colloidal matter are removed by the activated sludge process and suggests that the reactions take place in two steps. For the first they suggest the term bio-precipitation while the second step is one of oxidation and nitrification.

Since the discovery of the activated sludge process several theories

[35] *The Role of Bio-Precipitation in Sewage Treatment*, Thesis by R. A. Shive, Univ. of Ill., 1925.

have been advanced to account for the high nitrogen content of the sludge. Mohlman [36] suggested that the high nitrogen value of activated sludge was obtained by complete removal of suspended matter and by the "burning out of carbon." Richards and Sawyer [37] have attributed the extra nitrogen in activated sludge, over and above that found in the old type of sludges, to be due to initial absorption of soluble ammonium salts by the sludge, with subsequent assimilation by ammonia-fixing organisms. Experiments conducted by this laboratory [38] support the views of Richards and Sawyer. Our results showed that nitrates, nitrites and free ammonia were taken up by the organisms of the sludge and re-synthesized into protein for otherwise our nitrogen balance sheets would have shown a loss. Ardern, Jepson, and Gaunt [39] drew the conclusion that the high nitrogen of activated sludge is accounted for mainly by the flocculation of the sewage colloids and secondly in the growth of bacteria and higher organisms. However, they obtained no evidence from their experiments that the increase of the nitrogen of the sludge is due to the absorption and fixation of soluble ammonium salts. In all the previous work done along this line very little attention has been paid to the nitrogenous materials in true solution, other than the ammonium salts, nitrites and nitrates.

Hatfield [40] has made some very interesting calculations to show that the insoluble nitrogen of the feces alone is enough to account for the high nitrogen content of activated sludge. Adler [41] believed that normally, whatever the diet may be, most of the nitrogen is present in the feces in a coagulable form and that a very considerable part of it can be attributed to the intestinal bacteria. If the physical theory [42] for the mechanism of the activated sludge process is accepted, then it is difficult to avoid the conclusion that the coagulation of the fecal matter accounts for the high nitrogen content of activated sludge, but in the light of the biological theory for the mechanism of the activated sludge process it would seem advisable to consider the part played by such water-soluble nitrogenous materials as amino acids, urea,

[36] Mohlman, F. W., "The Activated Sludge Method of Sewage Treatment," *Illinois State Water Survey Bull.* **14**, 75 (1917).

[37] Richards, E. H., and Sawyer, G. C., "Further Experiments with Activated Sludge," *J. Soc. Chem. Ind.*, **41**, 62T (1922).

[38] "Activated Sludge Studies," *Illinois State Water Survey Bull.* **18**, p. 80.

[39] Ardern, E., Jepson, C., and Gaunt, P., "Recovery of Nitrogen from Sewage in the Activated Sludge Process," *J. Soc. Chem. Ind.*, **42**, 230 T (1923).

[40] Hatfield, W. D., "The Fertilizer Value of Activated Sludge," *Ill. State Water Survey Bull.* **16**, p. 120.

[41] "The Feces of Children and Adults," by Cammidge, P. J., 1914, p. 191.

[42] Eddy, *loc. cit.;* Fowler, *loc. cit.*

creatinine, albumins, globuline, proteoses and peptones in increasing the nitrogen content of activated sludge. Amino acids, although in small quantities, may be introduced into the sewage with the feces and the urine. Urea and creatinine, the most abundant nitrogenous substances in normal urine, are other soluble products which are passed into the sewage from the human body. The last four substances mentioned above are excreted from the human body only under abnormal conditions, but find their way into sewage from sinks and in nitrogenous industrial wastes such as wastes from canneries, slaughter houses, corn products plants, etc.

Urea is very quickly hydrolized by bacteria into ammonium carbonate and in this form it is available for assimilation by ammonia-fixing organisms of the sludge.

Food material in a soluble form is more easily assimilated by bacteria than in the solid form because it is necessary for the solid food to be liquefied before it can pass through the wall of the bacterial cell. There is no reason for assuming that the soluble substances cannot be re-synthesized into the protoplasm of the microörganisms as well as the solid suspended matter.

To further demonstrate the occurrence of bio-precipitation Shive with Buswell [43] cultivated *B. subtilis* in pure culture in large flasks of peptone broth maintaining a vigorous agitation throughout the incubation. At the end of the incubation the growth of subtilis was allowed to settle and the supernatant liquor analyzed.

Microscopic examinations and pH determinations were made on liquor from the three series of cultures (24, 48 and 72 hr.) set up. The results of this work are shown in Table 42 along with the percentage of total nitrogen precipitated. The various concentrations of broth that were used are expressed in terms of their total nitrogen content. It is seen from the latter table that the maximum precipitation of nitrogen in each case took place during the first 48 hours of aëration. After 48 hours spore formation set in or the cells began to break up, with the result that part of the nitrogen of the cells went back into solution and part remained suspended in the form of bacterial cells in the supernatant liquor and would not settle out.

Observations of spore formation, indicated in the table, furnish evidence for the support of the theory that spore formation is due to lack of food rather than the accumulation of products of metabolism.

[43] *The Rôle of Bio-Precipitation in Sewage Treatment.* Shive, Thesis, Univ. of Ill., June, 1925.

During the first 24 hours of aëration no spores were formed in any of the concentrations of broth used. At the end of 48 hours spore formation had progressed rapidly in the lower concentrations but no spores were present in the concentration having a nitrogen content over 500 milligrams per liter. At the end of 72 hours all of the concentrations showed that nearly all of the vegetative cells had changed over to spores, with the exception of the culture in full strength broth which had not yet shown evidence of spore formation although the chains were rapidly breaking up. Spore formation did not occur in the latter culture until the fourth day of aëration.

TABLE 42.—*Bio-Precipitation by B. Subtilis.**

Total Nitrogen, mg. per liter	pH	Spores	Percent of total nitrogen precipitated
		24 hours	
61.37	7.4	—	1.5
142.80	7.4	—	6.4
589.71	7.8	—	4.7
1223.77	8.4	—	6.2
		48 hours	
59.25	8.2	++	7.7
119.77	8.4	++	8.4
578.75	8.2	—	17.1
1223.75	8.6	—	12.9
		72 hours	
65.46		+++	0.0
118.90		+++	1.8
494.32		+++	8.6
1196.52		—†	7.7

*Shive with Buswell, *Univ. of Ill. Thesis*, 1925.
† Spores did not form until the 4th day of aëration.
Key:
— No spores.
+ Few spores.
++ Many spores.
+++ Nearly all spores.

In these experiments the "bulking" of activated sludge frequently observed by plant operators [44] has been duplicated under completely controlled conditions. In this case the phenomenon was clearly due to the age of the culture. Whether the same cause is effective with the mixed growths found in practice remains to be demonstrated.

[44] Shenton, *Report to City of Manchester, Rivers Department*, March 31, 1921; and *Eng. Contr.*, **40**, 79.

Fertilizer Value of Activated Sludge.

One of the attractive features of the activated sludge process has been the high nitrogen content of the sludge and hence its value as a fertilizer. Bartow and Hatfield [45] made an extensive investigation of this subject and demonstrated by pot cultures that activated sludge had high manurial value. They compared it with other sewage sludges in Table 43.

TABLE 43.—*Nitrogen Content of Various Sludges.**

	Organic matter	Total nitrogen	P_2O_5
	Percent	*Percent*	*Percent*
Septic tanks	29-54	1.1-2.9	...
Emscher tank	38	1.2	...
Filters—intermittent	...	1.45	0.78
Chemical precipitation	...	1.28	0.98
Grossmann's process	35	1.5	5.5
Globe fertilizer	43	1.65	1.71
Miles acid	...	2.7 to 3†	...
Milwaukee activated sludge	...	4.5‡	1.75
Urbana activated sludge	75	6.3	1.44
Urbana activated sludge	...	4.59	...
Chicago packing house waste	...	4.59	2.

* Bartow and Hatfield, *Ill. State Water Survey Bull.* 16, p. 91.
† Calculated from NH_3 to N_2.
‡ Calculated as N_2.

The sludge obtained at Milwaukee, Wisconsin, is of somewhat higher nitrogen content as reported by Kadish.[46] A typical analysis of Milwaukee sludge, which will be practically uniform in composition at all times, is as follows:—

	Percent
Moisture	6.20
Total nitrogen as ammonia	7.42
Water-soluble nitrogen as ammonia	1.13
Active water-insoluble organic nitrogen as ammonia (alkaline permanganate method)	4.17
Availability of water-insoluble organic nitrogen	66.35
Total availability of nitrogen	71.48
Total phosphoric acid	2.36
Potash (water-soluble)	0.13
Fat	4.87

The amount of sludge obtained is given by Pearse [47] and shown in Table 44.

Drying of Activated Sludge.

One of the most serious problems in the development of the activated sludge process has been the handling and drying of the sludge.

[45] *Ill. State Water Survey, Bull.* 16, p. 91.
[46] *Trans. Intrnl. Conference Sanit. Eng.* 1924, p. 134.
[47] *Ibid.*, p. 128.

TABLE 44.—*Data on Activated Sludge from Tanks in Various Cities in the United States (Dry Basis).**

	Pounds per million gallons	Composition			
		Fixed	Volatile	Nitrogen	P_2O_5
		Percent	*Percent*	*Percent*	*Percent*
Urbana	740 to 1150	...	...	5.1	3
Indianapolis	1152 to 1656	...	...	...	...
Milwaukee	2000	37.1	62.9	4.64	2.3
Houston	....	37.1	62.9	4.64	1.9
Chicago Sanitary District					
Packingtown	1900 to 2400	37.4	62.6	4.2	2.7
Tannery	2260	50.6	49.4	2.2	...
Corn Products	785	25	75	6.0	5.5
Calumet	400	...	...	4.5	...
DesPlaines	650	45	55	5.0	4

* Pearse, *Trans. Intrnl. Conference Sanit. Eng. 1924,* p. 134.

The sludge produced by the process is a biological jelly containing 96 to 99.5 percent of moisture. The water is combined with the gel to so large an extent that the ordinary physical means such as draining, settling, centrifuging, or filter pressing are relatively ineffective. Treatment with various chemical reagents which are known to cause gels to shrink and extrude water makes it possible to filter this material by means of pressure or vacuum filters to a cake of 70 to 85 percent moisture. From this point it must be dried with heat.

The chemical treatment of the sludge to prepare it for filtration has been the subject of numerous investigations particularly in the United States and in England. Bartow and Hatfield [48] tried a variety of reagents. They found that sulfuric acid when added to a pH of about 4.5 greatly increased the rate of filtration but that even better results were obtained with aluminum sulfate. Later investigations, a mere bibliography of which would require considerable space, have only served to confirm and make more specific these conclusions. Mohlman [49] finds the necessary dose of aluminum sulfate to be from 4 to 10 pounds per thousand gallons of sludge containing 98.5 percent moisture. The treatment with alum was far more effective than treatment with sulfuric acid (3.5 to 5 cc. per gal.).

Theoretically it is assumed that the aluminum ion combines with the "solution link" groups of the organic gel, lessening their tendency to bind water. The acid treatment is based on the assumption that

[48] *Loc. cit.*
[49] *Ind. Eng. Chem.*, 18, 225.

the gel is sufficiently uniform in composition to have a definite isoelectric point or point of minimum swelling.

In spite of all that has been done the drying of activated sludge remains a problem and the cost is greater than the market value of the fertilizer obtained. In some cases it will be necessary to carry this loss as a charge against the cost of sewage treatment.

Digestion of Activated Sludge.

This sludge when allowed to digest follows much the same course as that taken by fresh sewage solids. The amount of methane per capita should be increased by about 100 percent, since about twice as

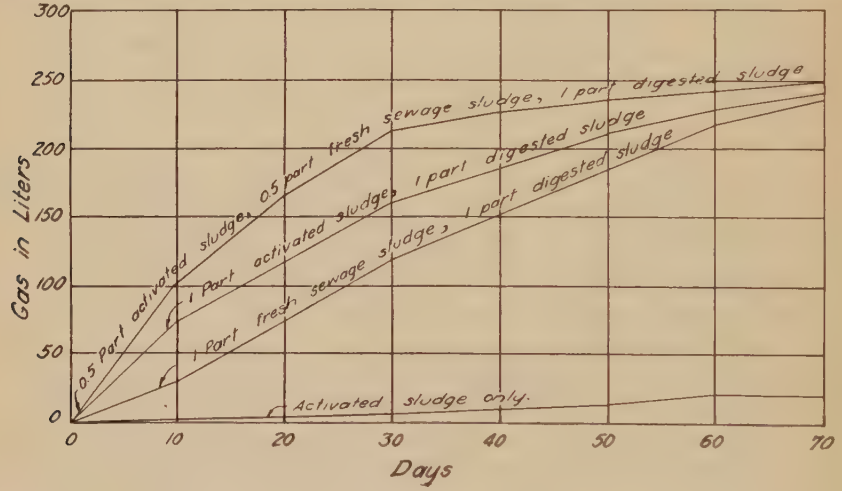


FIG. 53.—Gas from Digestion of Activated Sludge.

much insoluble organic matter is produced by the activated sludge process as is obtained by sedimentation. Imhoff [50] reports favorably on the combination of sedimentation and activated sludge with the combined digestion of settled and cultured sludges including arrangements for the collection of methane. Figure 53 summarizes his results.

Need for Intermediate Method of Treatment of Sewage.

Both activated sludge and sprinkling filters produce effluents of very high quality, often carrying less organic matter than the streams into which they are discharged. Tanks, on the other hand, remove only a third of the organic matter. There are many cases where an

[50] "Disposal of Excess Activated Sludge by Digestion," *Eng. News-Record*, 94, 936 (1925).

intermediate degree of purification would be satisfactory. Partial treatment with filters is impracticable but partial treatment with activated sludge has been employed to relieve the load on trickling filters.

An intermediate device between activated sludge and trickling filters is also needed. In the filter the amount of active surface per cubic foot is low while in activated sludge it is high (*see* Chapter XXII). An activated sludge plant of given capacity is from one-tenth to one-fifteenth as large as a tank and filter installation of like capacity.

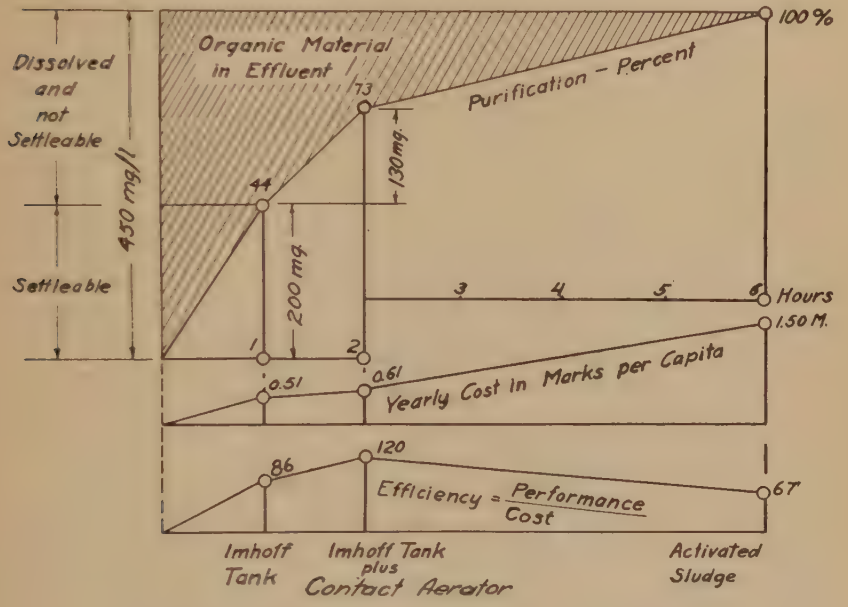


FIG. 54.—Efficiency of Contact Aërators (after Imhoff).

The operating costs of the former are high as is also the construction cost of the latter. A device more compact and less costly to build than filters and not expensive to operate would find wide use. The colloiders of Travis, lath placed in the sedimentation chamber on six- to nine-inch centers, represented a step in the right direction. But the amount of surface was small and the accumulated growths became septic and redispersed. The lath filters of Black and Phelps were subject to the same limitation. Many filters made of rather fine-grained material have been used in experimental and large scale installations from time to time but have not come into general use because of the danger of clogging. Brushwood has frequently been

employed. Favorable results were reported on a large brush filter in Toronto.[51] Richards and Weeks[52] have experimented with straw filters and Buswell[53] is operating a small corn cob filter. Woody vegetable material will decompose in time and at present data are not available to determine whether the cost of replacement will offset the saving in cost of installation. A recent experiment with an aërated sand filter was reported by Basiakine.[54]

Shive and Buswell[55] have described an experimental device so arranged that 20 square feet of active surface was available per cubic foot of tank volume. Provision was made to shake or agitate the active surface at intervals of about eight hours in order to remove the accumulated growths. Circulation and aëration were obtained by means of compressed air, the amount used being less than 0.1 cubic foot per gallon. A removal of 30 to 50 percent of the colloids was reported. The devices were referred to as "nidus racks."

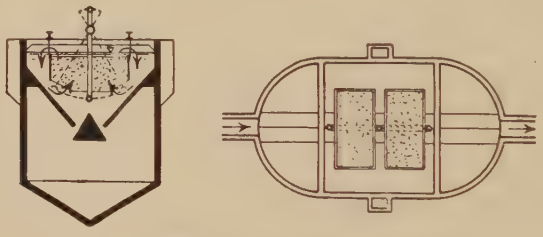


FIG. 55.—Imhoff Tank and Contact Aërator.

Imhoff[56] has recently described a similar device which he calls "Tauchkörper" or "contact aërators." The middle third of the sedimentation chamber of an Imhoff tank is filled with brushwood, underneath which an oscillating aërator introduces compressed air. The intermittent aëration removes the growth accumulations which settle in the last third of the chamber. Using 0.1 cubic foot per gallon Imhoff obtains about the same degree of purification as was obtained by Shive and Buswell. Figure 54 by Imhoff gives the relative efficiency of this method. Five installations of this sort are being built in the Ruhr District.

[51] *Eng. Rec.*, **75**, 376.
[52] *J. Soc. Chem. Ind.*, **40**, 252R.
[53] *Eng. Contr.* **65**, 2 (1926).
[54] *Report of the Commission of Moscow, 1925.*
[55] *Loc. cit.*
[56] "Submerged Contact Aërators for Sewage Treatment," *Eng. News-Record*, **97**, 24 (1926).

Chapter XXII.

Microbiology of Colloid Removal.

Microbiology of Sewage Filters.

As indicated in the previous discussion there are two groups of reactions which take place in trickling filters, (*a*) bioprecipitation and (*b*) oxidation or nitrification, as the latter is usually called. Bioprecipitation is accomplished by larger organisms, the chlamydobacteriaceae or "giant bacteria," the fungi (especially molds), the larger protozoa, and certain higher animals. These organisms are found to compose the bulk of the growth on the filter stones. A certain amount of oxidation is accomplished incidentally by these organisms since they give off carbon dioxide. They also break down nitrogenous organic matter with the formation of ammonia in some cases and to that extent aid the second or nitrification process.

Early Development.

During the earlier development of sewage filters several investigations of their microscopic population were made.[1] In 1914 J. W. Haigh Johnson summarized the results of his own and other investigations in an extensive article from which we shall quote.[2]

> Long before Frankland's time it was known that when organic nitrogenous bodies are applied to the soil, the nitrogen becomes eventually converted into nitrate, but it was reserved to Muller in 1873 to indicate, and to Schloesing and Muntz in 1877 to demon-

[1] Kolkwitz, R., and Marsson, M., "Ökologie der pflanzlichen Saprobien." *Ber. deut. botan. Ges.*, 26a, 7 (1908); "Ökologie der tierischen Saprobien." *Intern. Rev. gesam. Hydrobiol. Hydrographie*, **2**, April, 1909; Marsson, M., "Die Abwasser-Flora und Fauna einiger Klaranlagen bei Berlin und ihre Bedeutung für die Reinigung Stadtischer Abwasser." *Mitt. kgl. Material-prufungsamt Berlin*, p. 4, 1904; Wilson, H. M., and Johnson, J. W. H., *West Riding Rivers Board Reports: (a)* "Biol. Examination of the River Wharf," Dec., 1910; (*b*) Biol. Work in Laboratory, Apl., 1910-Sept., 1911; Oct. 1911-Mar., 1913; Apl., 1913-Mar., 1914; (*c*) "Ecological Notes on *Sphaerotilus natans*," Kutz, Oct., 1911; (*d*) Biol. Rept. on the Balne Beck, Dec., 911; (*e*) Report on the Organisms Found in Sewage Filters, pt. **I**, July, 1913; pt. **II**, Apl., 1914; Davenport, M. W., "Physiological Control of Sewage Filters," *Eng. News* **60**, 117.

[2] "A Contribution to the Biology of Sewage Disposal," *J. Econ. Biol.*, **9**, 105-125, 127-163.

strate that this nitrification process is due to bacteria. In 1882, Warington showed that this change takes place chiefly in the upper six inches of the soil. The destruction of these organic matters is not entirely restricted to bacteria, and in 1883 Dr. Sorby clearly demonstrated this fact in his evidence before Lord Bramwell's Commission on the Metropolitan Sewage discharge. He showed that the sedimentary fecal matter in the River Thames disappeared, and was replaced by small rounded particles, which were excrement of Entomostraca. He also found large numbers of crustaceans (freshwater shrimps) and of small annelids and other mud worms actively devouring the deposits from the sewage, thus establishing the important fact that organisms of a higher order than bacteria act as sewage scavengers. In 1866 Dr. Dupré suggested the cultivation of such organisms and their discharge along with the polluting liquid.

As stated, nearly all investigations of the sewage problem seem for many years to have quite overlooked the function of the larger (macroscopic) organisms such as those mentioned by Sorby and Dupré; but in 1900, Dunbar drew special attention to the function of higher plants and animals, and later, in 1907, Höfer went more fully into the scope of their action. In 1904, Dibden also pointed out the large number of active insects and annelids at work on the mud deposited on the surfaces of the material in his slate beds.

The upper portion of a filter receiving crude sewage contains chiefly those forms of life which belong to the Polysaprobes (tolerant of pollution), and this zone is especially prolific in these lowly organisms. The filter material rapidly becomes coated with a slimy or gelatinous growth of *Zoogloea ramigera*, which may be regarded as a large number of bacteria embedded in a gelatinous matrix. This zoogloea is perhaps the most characteristic and important organism of this zone, and forms a suitable nidus for the development of fungal and other forms of life; whilst its gelatinous character enables it to directly absorb *soluble* polluting substances—as already described in Dunbar's absorption theory. *Sphaerotilus natans, Beggiatoa alba, Thiothrix nivea, Chromatium okenii, Polytoma uvella*, etc., may also occur while species of *Saprolegnia* and other higher fungi are often brought down the sewers and develop on the top of the filter, together forming a fairly efficient strainer. The numerous hyphae which are to be found in this mass are not readily identified, but *Mucor racemosus* and *Mucor circinelloides* can be frequently recognized in subcultures.

Botrytis vulgaris is also found in such situations; this fungus attacks cellulose very vigorously, and in one instance the growth was so dense that it very seriously obstructed a small water-course. Two characteristic chromogenic bacteria were also isolated from this material, *Magenta bacillus* and *B. violaceus*.

In some instances, however, where the discharges from modern industrial processes such as dyeing, carbonizing and brewing have given an acid character to the liquid, the filter may then become covered with an orange colored fungus, *Fusarium auriantiacum*,

and tufts of *Oospora lactis* may become very abundant. The former organism seems to be associated with the decomposition of carbohydrates, while the normal decomposition under neutral or slightly alkaline conditions is perhaps more intimately connected with changes in the nitrogenous contents of the sewage.

Some fungi are capable of existing under apparently very adverse conditions and *Sporotrichum lanatum*, Wall., was identified in material taken from the sill of a purification works treating dye waste. The material, although deeply stained with the dye liquids, was still alive and rapidly produced spores which led to its identification. Agarics rarely appear on sewage filters but *Hypholoma condolleanum*, Fr., has occurred on partially dried sludge in a settling tank, and often develops along with *Pilobolus* on the drying sludge.

The sub-aerial character of this zone markedly affects the range of organisms occurring in such a grossly polluted liquid, and organisms belonging to the mesosaprobes (moderately tolerant), such as *Phormidium autumnale*, which often forms a large bluish-black coating over a considerable portion of the surface and in summer dries up into blackish paper-like sheets, *Podura*, and the larvæ of *Psychoda*, *Chironomus*, etc., while birds, flies, spiders, snails and worms often abound. In addition to these larger forms of animal life, amœbae, infusorians (*Paramœcium*, *Vorticella*, etc.) and rotifers may occur in large numbers.

The flora and fauna of a filter also exhibit certain seasonal variations, the most noticeable being characterized by a change in the color of the filter surface, which is usually of a dirty gray or blackish slimy appearance. This change is generally attributable to the depredations of some form of animal life, e.g., "*Podura*" (*Achorutes viaticus*) which devours the accumulated deposits of slime, etc., on the filter material and thus reveals the natural color of the clean filter medium. This natural cleansing often commences at one point and gradually extends over the whole surface, and occurs chiefly in spring and autumn.

The flies found about such installations can scarcely be said to be restricted to any particular zone, but their eggs, larvæ, etc., are naturally most numerous near the surface which is directly available for the deposition of eggs. Besides the two species of Psychoda which are described later, *Spathiophora hydromyzina*, *Camptocladius arterrimus*, species of *Chironomus* and *Trichocera hiemalis* are of fairly frequent occurrence. Hitherto, 109 mature spiders have been examined from three works near Wakefield and the results obtained show such a remarkable dominancy of relatively rare species that a detailed list of their occurrence seems justified. The figures within the parentheses refer to males and females respectively:—*Erigone atra*, Bl., 4 (2, 2); *E. arctica*, White, var. *maritima*, Kul., 19 (7, 12); *E. dentipalpis*, Wid., 6 (3, 3); *E. promiscua*, Cb. 4 (2, 2); *Lessertia dentichelis*, Sm. Tmeticus simplex, F. O. P. Cb. 60 (7, 53); *Araeon-*

cus humilis, Bl., 1; *Porrhomma thorellii,* Herm., 15 (2, 13). It will be noticed that the three dominant species with their percentage occurrences are:—*Lessertia dentichelis,* Sm., 55; *Porrhomma thorellii,* 13.6; and *Erigone arctica v. maritima,* 17.4; these three species together constitute 86 percent of the total arachnida observed. The two former species are of distinctly rare occurrence in Britain, while the occurrence of the latter variety at such a distance from the sea is also interesting. The *Lessertia* appear to belong to the variety *sublucicola.*

Arion hortensis is perhaps the most frequent slug, and is doubtless attracted by the large amount of organic matter deposited from the sewage. In contact beds the rather rare leech, *Trocheta subviridis,* has at times occurred in considerable numbers.

Besides the bacterial forms already enumerated, free-swimming species such as *Colon bacillus, Spirilla,* and other putrefactive bacteria may be present in large numbers; the number of the latter depends chiefly on the amount of putrefaction which has been allowed to occur.

Opportunities for the examination of the organisms at any considerable depth below the surface of the filter have until recently but rarely occurred. Such information as is at present available indicates that the zoogloea masses rapidly become much less, while rotifers, paramaecia, nematodes and small earth-worms increase, and fungal hyphæ are still present in less quantity than nearer the surface. In cases where the treatment is performed by two filters in series a number of algæ have usually developed on the surface of the second, such as *Prasiola crispa, Stichococcus flaccidus, S. dissectus, Ulothrix variabilis, Myxonema tenue* (often with peculiar swollen cells); although "Podura" occasionally occurs, flies are relatively scarce. The deposit on the filter material loses its slimy character and becomes brown in color. This zone does not appear to have any outstanding characteristic, but functions as an intermediate between the other two. The next zone does not support many living organisms, most fungi have entirely disappeared, bacteria are much less frequent, while numerous worms and a rich brown deposit of humus are the chief indications of the final stage. Algæ would under normal conditions develop in such a liquid, but the absence of light within the filter precludes their development. The effluent channel, however, usually exhibits brown masses of small diatoms and green strands of algæ. *Van Heurckia rhomboides v. saxonica* (Rabh.), G. S. West, *Gomphonema parvulum, Achnanthes lanceolata,* and var. *dubia* are most common among the former, while species of *Mougeotia, Myxonema, Cladophora, Vaucheria, Rhizoclonium* and *Ulothrix* are of frequent occurrence among the latter. At times gray patches of *Carchesium lachmanni* may appear, and more especially if the effluent is occasionally of doubtful purity. It will thus be readily seen that the flora and fauna of a water-course provide indelible evidence of the *general* character and purity of the liquid in that water-course.

The Sewage-Fly or Moth-Fly (*Psychoda*).

All percolating filters serve to some extent as a breeding ground for flies of various kinds, and in consequence they are the favourite haunts of swallows, wagtails, and other small insectivorous birds. In the majority of cases these flies, although varying in numbers according to the season, are not so numerous as to make their presence obnoxious, at least beyond the confines of the sewage works. In other cases, where circumstances favor their development, they may appear in myriads at certain times of the year and be carried by the wind into inhabited neighborhoods so as to give rise to an intolerable nuisance.

This nuisance may be looked upon as causing annoyance:—(a) from the presence of the insects in such numbers in and about dwellings, where they are troublesome by reason of the personal discomfort they produce, and although not all persons are affected, it seems certain that in some cases, the flies or perhaps the readily abraded hairs produce great skin irritation; (b) by their unsightly appearance, attaching themselves as they do to any object, particularly any moist surface; and (c) by their settling upon articles of dress and food.

The flies which are chiefly responsible for this nuisance belong to the genus *Psychoda*, and appear to be chiefly restricted to the two species *Ps. phalaenoides* (L.) and *Ps. sexpunctata,* Curtis.

When a filter in which the top layer consists of large pieces of filtering material, or which has dry built side walls, is examined during warm weather these flies, their pupæ and their larvæ, are to be found in the interstices of the material. If a piece of material be removed from the top of the filter, the dry portion of its under surface is usually covered with the mature insects. These are small active brownish-gray hairy flies, with transparent wings and long and characteristically jointed antennæ. The wings are longer than the body, which they completely cover, and when at rest have a characteristic roof-like slope. Both the body and wings are densely covered with hairs, which give the fly at first sight the appearance of a small moth, and hence the name *Psychoda* (moth-like). The hairy covering on the wings and body offers considerable resistance to flight, and consequently movements are chiefly restricted to running, hopping, or short flights. The fly was very common in the old-fashioned unattended street urinals, flitting from slab to slab or running about their edges. It has a marked predilection for moist decaying animal and vegetable matter, and for malodorous moist situations in general. It is sometimes found in swarms in hot-houses and about open drains in spring and autumn. It must not, however, be concluded that Psychoda is restricted to polluted areas, for it occurs in the woods and forests far away from human surroundings.

The eggs are deposited in moist surroundings, and these of course are available in a sewage filter.

Recently attempts have been made to rear these insects artificially, and it was found that during warm weather the life-cycle was regularly completed within 17 or 19 days. During cold weather, however, this period was greatly increased.

The larva is extremely voracious and almost ceaselessly engaged in devouring food during the whole period of its existence, this food in the case of the sewage-fed larvæ consisting of deposited organic matter, fungal hyphæ and the zooglœa masses which develop upon the filtering material. In this mass of slime the larvæ move about with a worm-like motion, assisted by the action of their strong mouth parts. They can remain totally submerged for some considerable time without much inconvenience; food is often obtained whilst the head of the larva is buried in slime, for the respiratory apparatus is situated in the tail and this is raised above the surface, thus securing the necessary supply of air.

Headlee[3] has pointed out that complete flooding of the filter bed at fourteen-day intervals drowns out the Psychoda larvæ and effectually controls the multiplication of this organism in cases where it has become a nuisance.

The Water Springtail. *Achorutes viaticus (Linn.), Tullb.*

These small wingless insects, which were referred to as "Podura," are found on some filters quite as abundantly as the sewage fly, Psychoda, but, as previously stated, the two insects seldom appear together in profusion.

Springtails occur as bluish-black masses, most evident on small pools of ponded sewage on the filters or on the surface of a humus tank, where at first sight they remind one of small soot particles floating on the surface of the liquid. They may also be found in great profusion on the moist surface of the filtering material, often giving it a bluish-black appearance, and on drying masses of sewage sludge. Each insect is about 2 mm. or $\frac{1}{12}$ inch in length.

Parkinson and Bell ("Insect Life on Sewage Filters," Sanitary Publishing Co., 1919) have made an extensive study of this organism which in their experience prevented clogging or ponding. Ponding filters were cured by inoculation with *Achorutes viaticus*.

Dominant Algæ.—Where land is used for the final treatment of sewage, "ponding" is liable to occur, and in such cases green colored organisms often appear in such profusion as to color the liquid.

Species of *Chlamydomonas* and *Euglena* are amongst the most frequent, and in one instance a large area was similarly colored by *Richteriella botryoides;* chiefly of the *fenestrata* variety. This alga has only once been previously recorded in the British Isles—Lough Beg, Ireland—and it is doubtful if the variety has ever been obtained before in these islands. Its appearance, therefore, in such profusion is the more remarkable.

[3] *J. Econ. Ent.* **12,** 35.

Dr. Letts has shown that the marine alga, *Ulva latissima,* so common in the "sloblands" of Belfast Lough, possesses in a remarkable degree the property of rapidly absorbing soluble nitrogenous sewage matters. The same property is also exhibited by the green alga, *Prasiola crispa,* which, under suitable conditions, develops both in the thalloid and filamentous forms on the surface of sewage filters. The latter form often occurs as green filaments between the "setts" of the quiet streets in our towns, while the former is frequent on the bare moorland, where it is entirely dependent upon human source for its nitrogenous supply.

Recent Investigations.

Of the more recent investigations in the ecology of sewage filters the most extensive is that carried on at the Sewage Substation of the New Jersey Agricultural Experiment Station and reported in their four annual reports of 1922 to 1925. The following extracts summarize their findings.

(Crozier 1922 Report.) The list of organisms identified in the film includes no types unknown in polluted natural waters. The origin of the population of the film must be referred to the normal water supply. For example, the genus Aspidisca is represented by the two species common in streams and ponds in this vicinity. Similar considerations apply to the other types listed. Those creatures which may be carried into the sewage filter, and which find there conditions permitting their residence and growth, become the characteristic inhabitants of the film. The filter is a kind of concentrated, telescoped, natural stream.

These studies of the animal census of the film give no direct support to the conception that protozoans, for example, or other animal types, are directly concerned in sewage purification. There is every reason to regard this as primarily a function of bacteria. The animals are probably of greater significance for a filter film in connection with their locomotor activities, maintaining the film in a porous condition; and in the case of attached forms by their providing a structural frame-work for the film. Annelids in particular are intimately connected with the self-regulatory sloughing of the film. The cyclic character of the sloughing process is to be considered in terms of the animals involved and their sequential variations.

(Hausman 1923 Report.) The surface layer of stones were covered throughout the year with an abundance of a green alga, Stigeoclonium, and the blue-green alga Oscillatoria. A relatively small amount of fungi were present on the surface stones. On the subsurface stones the slimy film was bound together largely by fungi, Beggiatoa, filamentous bacteria and stalked protozoa. The principal fungi found in the mycelial stage were Penicillium sp., Pythium sp., Dictyuchus and two unidentified forms, one of which is probably

an Oïdium. Beggiatoa and the filamentous bacteria have a seasonal fluctuation opposite that of fungi, reaching their maximum during the summer and a minimum in winter. Fungous hyphæ seem to play an important rôle in building up and binding together the film on the subsurface stones of the filter bed.

(Rudolfs and Trajkovich 1924 Report.) There is a seasonal fluctuation of the fungi, reaching a maximum during the winter months and a minimum during June, July and August. It is pos-

Fig. 56.—Seasonal Succession of Organisms in the Filter Bed Film (after Rudolfs *et al.*).

sible that the increased temperature has a direct influence upon the disappearance of the fungi; it is also possible that the increased efficiency in nitrification of the bed during this time is a factor, especially in view of the fact that inorganic nitrates are not available for the penicillium experimented with in the laboratory. The relation between the average temperature of the sewage just before it is thrown on the bed and as it leaves the bed and the fluctuation of total fungi for all levels in the bed supports this view.

(Lackey 1925 Report.) Filter bed studies have included a number of new points this year. The cause of sloughing has been spoken of at various times and some investigation of it has been made. As the tiles from the cabinet which was sunk in the bed this past year should have given some light on this question, a special

procedure was inaugurated with this end in view. It was early noted that the sewage was trickling in a fairly even manner over the tiles which should have given an even coating of film. Accordingly the film from six tiles (two tiles each from one-, three-, and five-foot levels) was scraped weekly, and an examination of their fauna was made as often as was deemed necessary. The weight of this weekly film collection was noted (wet basis); later the same procedure was changed to a collection once in two weeks. The "wet weight" of this film is water-saturated material. The second part of this procedure consisted of taking similar film samples from tiles which had been in the bed since the beginning of the experiment. Comparison of the weights thus obtained were made.

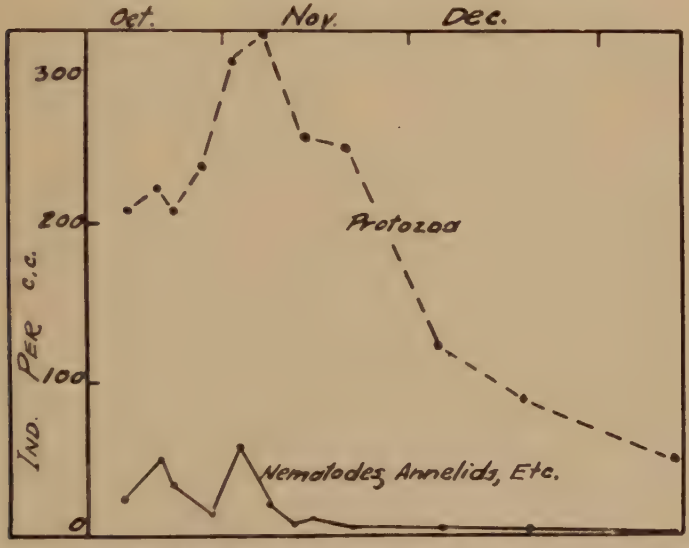


FIG. 57.—Organisms in Filter Effluent During an Autumn Sloughing Period in Number of Individuals per cc. (Rudolfs *et al.*).

The results were not according to expectations. In the first place weekly accumulations showed surprising fluctuations. This was apparent even for the three levels, as shown by the figures for the one- and five-foot levels in Table 45. There were even greater fluctuations in the film weights for tiles from which film had been collected but once. This suggested an uneven trickling of the water, but repeated inspections of the tiles in situ failed to confirm this at least for the first few months.

In the course of time, however, a heavier film gradually accumulated on those tiles which had been longest in the rack. Perhaps the most notable thing in this connection was that the film texture from these tiles was very different from that of tiles cleaned every

week. The film deposited in a week was thin, white or gray, and very gelatinous—a true zoogloœa. The older film was thicker, blacker, and had a firmer consistency. One could note three regions. The outer layer was a zoogleat, thin with a whitish color. This adhered to the middle layer, which was thin and crust-like, apparently forming a substratum for the outer region. Underneath this was the inner layer, which was like a thin black ooze or mud. There was some grit in this layer.

The water content of the film was always very high. Upon evaporation a gradual increase in the dry weights of the film was shown. Incineration showed that the greatest increase was due to the inorganic material. Apparently it accumulated about three times

TABLE 45.—*Animals Present in Film One Week and Ten Weeks Old, at Various Depths.*

	Film 1 week old	Film on tiles since slough, 10 weeks old
	Per cc. of film	Per cc. of film
One-foot level:		
Opercularia	349.8	189,700
Minute flagellates	594.2	471,700
Colpidium	220.4	28,600
Chilodon	47.1	25,400
Vorticella	6.4	.....
Pleuronema	1.3	.....
Glaucoma	1.3	3,200
Menoidium	1.3	.....
Amœba	648.7	307,400
Cochliopodium	.....	3,200
Lionotus	.....	1,300
Cyclidium	.....	3,200
Five-foot level:		
Opercularia	66,100	169,600
Minute flagellates	305,300	296,800
Colpidium	20,400	7,400
Chilodon	156,000	42,400
Vorticella	3,400	1,100
Pleuronema	45,800	18,000
Glaucoma	10,200	1,100
Amœba	551,200	286,200
Lionotus	.....	13,800
Cyclidium	5,100	11,700
Menoidium	.....	2,100
Aspidisca	.....	2,100
Lembus	.....	1,100
Trimyema	.....	1,100
Difflugia	.....	1,100
Petalomonas	.....	1,100
Chlamydophrys	.....	5,300
Peranema	.....	1,100
Cinetochilum	.....	1,100
Actinophrys	.....	2,100
Euglena	.....	1,100
Entosiphon	.....	1,100

as fast as did the organic matter. The composition of the organic matter however would make this a reasonable figure, for the organic matter represents such substances as cellulose and chitin in the stalks and pellicles of algæ, fungi, bacteria, protozoa, rotifers, and the other inhabitants of the film. Such materials would not necessarily accumulate as would the grit. This led to a study of the faunal differences between the two kinds of film. Table 45 gives a comparison of film a week old with film ten weeks old. The older film has more varieties of organisms in it, but they are far fewer in numbers per cubic centimeter. An exception must be made in the case of the nematodes and rotifers, and apparently of the annelid worms. But all of the film which is a week old is habitable for the animals; in fact, they largely make up the film. Of the old film only the outer layer is habitable by the protozoa and most of the other forms. This is due to the fact that most of the food is available nearest the surface, where the oxygen supply is. In the third layer—the innermost one—are found numbers of active metazoan forms, for they are strong enough to writhe their way through this layer and to get to the surface layer when they need oxygen. They appear to inhabit this lower layer enough to keep it porous.

Large quantities of film, mostly various fungi unknown to the zoologist, were present during the winter months. But the numbers of Metazoa were low during all this time. In June came the spring slough and the beds were cleared without any large numbers of rotifers, nematodes, or annelids ever having been present. The writer regards the slough as a simple matter of seasonal succession of fungi and a gradual accumulation of detritus. Chemical analyses have shown that nitrification is best shortly after sloughing and decreases gradually with the increase in thickness of the film. The importance of finding means to keep the film layer at its optimum efficiency is thus apparent. The keeping of the film at its desired thickness will involve a more intensive study of the physiology of fungi and of animals present and the necessity of knowing how to effect the control of their growth.

It was proposed to catalogue and illustrate all of the known forms found in the study of sewage disposal. This report completes the known filter bed Rhizopods. The list of them is as follows:

Protameba primitiva
Amœba proteus
Amœba radiosa
Amoeba verrucosa
Hartmanella hyalina
Vahlkampfia albida
Vahlkampfia guttula
Vahlkampfia limax
Difflugia pyriformis
Cochliopodium bilimbosum
Arcella vulgaris
Arcella dentata
Centropyxis aculeata
Euglypha alveolata
Trinema lineara
Pamphagus mutabilis
Chalmydophrys stercorea
Actinophyrs sol
Actinosphaerium eichornii

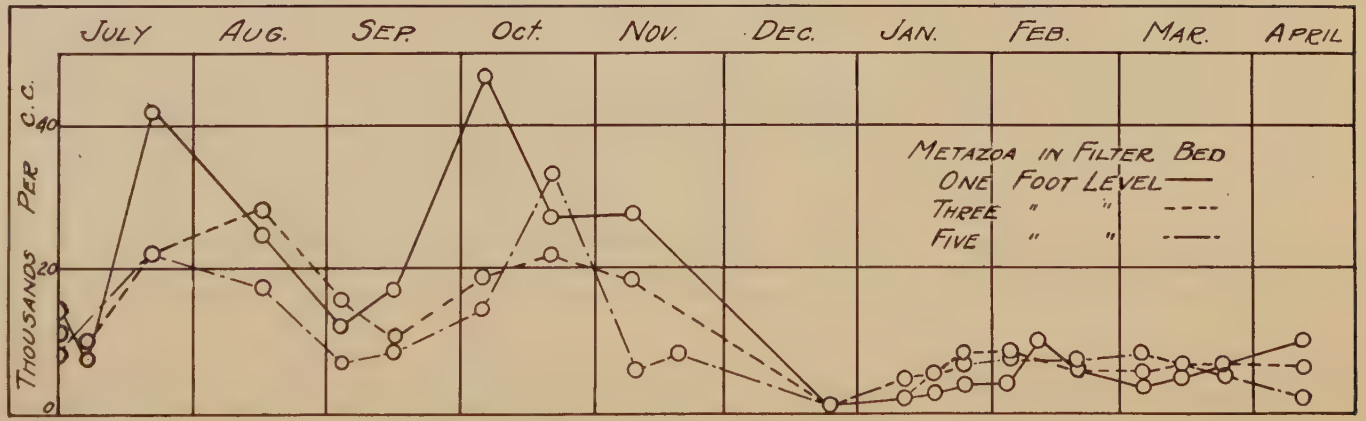


FIG. 58.—Metazoan Succession in Sprinkling Filter Bed (Rudolfs *et al.*).

Of various other studies of this subject reference may be made to the following: Algae Growths Cover Atlanta Sewage Filters by Charles C. Hommon; One Ton of Leathery Material removed from 2.5 acres of beds. *Eng. Record*, 72, 335, 1915; Non-Bacterial Population of Sewage Trickling Filters by C. R. Cox, *Eng. News-Record*, 87, 720 (1921).

A study of the bacterial population of sewage filters has been made by Hotchkiss.[4] She made a study of the groups of bacteria present by means of the dilution method. She concluded as follows:

> In the filter bed a change suggestive of decreasing oxygen tension is seen. The nitrate-reducing organisms occupy a larger place as the samples are secured deeper in the bed. The albumin digesters also increase and the numbers in the lower levels seems to influence the character of the effluent. These organisms make up 7 and 8 per cent of the bacteria found in the first and second pipes which are 1 and 3 feet from the surface of the bed and 15 per cent of the bacteria in the third pipe which is 5 feet below the surface, while the effluent which drains from the bed contains 24 per cent of these organisms. In contrast to the increase in this type of proteolytic organism in the filter bed it seems that the flow of sewage through an Imhoff or settling tank does not increase the predominance of the albumin digesters. The organisms form 7 per cent of the influent and 4 per cent of the effluent of the Imhoff tank. They have increased to 24 per cent in the filter effluent and yet the final effluent contains only 6 per cent. Perhaps these organisms find their most favorable habitat around undissolved protein material which tends to sink and so to rid the liquid of the proteolytic organisms.
>
> The filter bed has been regarded as the site of oxidation changes which tend to render the effluent stable and inoffensive. If the sulfur cycle is considered it will be noted that the producers of hydrogen sulfide from protein which form 51 per cent of the bacteria in the filter influent from the top layer of the filter bed decrease until there remain only 7 per cent in the filter effluent. The group of organisms which produce hydrogen sulfide from inorganic sulfates are less numerous. They form 2 per cent of the bacteria in the liquid of the upper level of the filter bed, increase to 5 per cent in the middle layer, decrease to 1.8 per cent in the lower layer while the filter effluent contains 0.7 per cent. In other words, these hydrogen sulfide producers tend to be eliminated also. Turning to the sulfur oxidizing bacteria, those which grew under our cultural conditions formed only 0.5 to 0.3 per cent of the bacteria in the liquid from the filter bed; however, the effluent from the filter bed contains 3 per cent and this indicates an increase of

[4] *J. Bact.* 9, 437.

these organisms. It is, then, the tendency of hydrogen sulfide producers in the filter bed to decrease in numbers but the sulfur oxidizing bacteria increase. In spite of such a tendency the oxidizers do not increase to such an extent that they become of great numerical importance.

In considering the nitrogen cycle it will be remembered that the nitrifying organisms are divided into two groups—those which produce nitrite from ammonium salts and those which utilize the nitrite and form nitrates in so doing. The nitrite producers are here the more numerous group. They form 1 per cent of the organisms in the liquid from the upper layer of the filter bed, 5 per cent in the second layer, 3 per cent in the third layer and 0.7 per cent in the effluent. The nitrate producers form only 0.2 per cent of the bacteria in the liquid from the upper layer, 0.4 per cent in the second layer and 0.9 per cent in the third layer. The effluent contains 1 per cent.

In spite of the increase in nitrate nitrogen in the filter bed our bacteriological studies show that the nitrate reducing bacteria are predominant. These organisms form 50 per cent of the bacteria in a cubic centimeter of filter liquid, while the nitrifying organisms form 3 per cent of the bacterial population in the same location. The filter effluent contains 62 per cent nitrate reducers and 1.7 per cent nitrifiers. The liquid from the digestion chamber contains 57 per cent of nitrate reducers and 0.78 per cent of nitrifiers. The ratio of the nitrifiers to the nitrate reducers in the three locations is 0.059, 0.027, 0.013. Therefore it seems that conditions in the filter bed are such that the nitrifying organisms multiply more rapidly than in other parts of the disposal plant. It has been suggested [5] that one factor is the partial digestion of organic matter to simpler forms which are more readily attacked by the nitrifying organisms. This may account for the fact that nitrification is greater in the lower levels of the bed although *a priori* it would seem that oxygen tension deeper in the bed would be less favorable for oxidation changes.

TABLE 46.—*Bacteria in the Film of a Sprinkling Filter.** *Geometric averages of bacteria per gram of dry film.*

	Surface	1-foot level	3-foot level	5-foot level
Nitrate reducers	964,000	174,000	96,200	1,524,700
H_2S producers (protein)	600,100	36,281,000	5,522,200	1,444,500
Albumen digesters	1,177,900	933,000	1,435,000	1,313,300
H_2S producers (sulfate)	2,854,100	272,000	528,200	361,000
Sulfur oxidizers	66,100	632,500	1,130,100	1,444,500
Nitrite producers	39,900	1,205,000	1,394,300	2,335,500
Nitrate producers	4,000	9,000	13,900	311,400

* New Jersey Exp. Sta. Bull. (1923).

[5] New Jersey Exp. Sta. Bull. 390 (1923).

Microbiology of Activated Sludge.

J. W. H. Johnson [6] appears to have been the first to report on the microscopic growth of activated sludge. His findings in brief are as follows:

> Microscopically, the bulk of the mud (sludge) shows nothing very characteristic, but the repeated presence of *Opercularia* suggests an association which I have noticed in rapidly flowing water where *Zoogloea ramigera* was the dominant organism, and from experiments now in operation it seems possible that zoogloea, assisted by other minute organisms chiefly of animal origin, may be responsible for the rapid purification thus effected. That such minute animal life, i.e., protozoa, rapidly destroy nitrogenous substances is proved by the increased amount of nitrogen and its derivatives observed when soil is partially sterilized, and the protozoa are thus destroyed.
>
> Whatever may be the *modus operandi* of this purification, the process has been developed along lines of natural biological evolution; each improvement in the method of aëration has produced a corresponding increase in the number and the variety of organisms which were capable of participating in the oxidation of the polluting organic matter, and has thus given an increased efficiency.

Some of the earlier writers make especial mention of nitrifying bacteria. Bartow and Smith [7] noticed large numbers of worms (Aeolosoma Hemprichii) as well as Vorticella and Rotifera at times in the sludge. Purdy [8] counted the various protozoa in strawboard waste activated in a 3-inch glass tube and fed by the fill and draw method.

More recently Dienert [9] and Cambier [10] have debated the rôle of bacteria in the activated sludge process. Dienert maintains that bacteria are essential, since nitrification did not take place in the presence of phenol. Cambier on the other hand maintains that the activated sludge process is an example of ordinary chemical catalysis. His conclusions appear to be based on three experiments: one in which chloroform was introduced with the air used for aëration, apparently on the assumption that the chloroform would be a germicide; one carried out at low temperature (10°-12° C.) on the assumption that nitrifying bacteria are not active at these temperatures; and one in which iron sulfide was added. That nitrification and purification were accomplished under these conditions Cambier interprets as proof of the catalystic theory of the reaction. He presents no definite data, however, to show sterility of his solutions. In the same journal Courmont [11] reports a study of the

[6] *Loc. cit.*
[7] *Ill. State Water Survey Bull.* **13**, 329.
[8] *U. S. Pub. Health Service Bull.* **97**, 45.
[9] *Compt. Rend.* **170**, 762, 899; **173**, 184.
[10] *Compt. Rend.* **170**, 417, 681; **171**, 57.
[11] *Ibid.*, **170**, 75, 976, 1134; **172**, 1696.

bacterial flora of activated sludge effluent. He found seven species, one of which was B. subtilis. No obligatory anaerobes were found and in some cases B. coli was absent.

Richards and Sawyer [12] have recently presented data including chemical analyses, bacteria counts and microscopic determinations of the number of protozoa. A relation was established between the number of protozoa and bacteria, and the high nitrogen in the activated sludge was attributed to synthetic living protein of the bodies of bacteria and protozoa. Under certain conditions of aëration free ammonia and nitrates were synthesized into proteins, as contrasted with the formation of free ammonia and nitrates which is ordinarily observed in the activated sludge processes.

Purdy [8] followed the usual Sedgwick-Rafter method for enumerating the microscopic organisms, reporting the zoogloeal flocs in standard units of 0.0004 sq. mm. He used a 500 cc. aërating vessel operated with an unmeasured excess of air on the fill and draw system with 24-hour aëration periods. This system served admirably the purposes of the particular investigation which showed the presence of relatively large numbers of protozoa, especially of Peritrichs. Some work of the present author on a similar scale and with excess of air and 24-hour fillings gave similar results. They do not seem to correspond to results obtained when smaller amounts of air are used, nor with the results on larger experimental units.

Buswell and Long [13] have studied the organisms of activated sludge from both qualitative and quantitative standpoint. Their report follows:

> The analytical data herewith reported refers to samples taken from the aëration chambers of a two-tank activated sludge unit fully described elsewhere.[14] For the purpose of the present paper it will be sufficient to state that the apparatus was treating about 65,000 gallons per day in two aëration chambers having capacities of 14,400 and 12,700 gallons respectively and operated in series. Approximately 0.75 cubic foot of air was used per gallon, of which two-thirds was used in the first tank and one-third in the second. A good degree of clarification and an average methylene blue stability of three days were obtained during the run.
>
> Microscopic observation made during the winter of 1920-1921 indicated a relation between the amount of air used, the strength of the sewage, the settling rate of the sludge and the types of organisms composing the sludge. When in the spring, after a shut down for repairs, the plant was started up without any activated sludge as a "starter," daily microscopic observations were made to follow the changes in microbial life as the sludge built up. The daily records are given below. In general it is to be noted that the Holotrichs were

[12] *J. Soc. Chem. Ind.* **41**, 62T (1922).
[13] "Microbiology and Theory of Activated Sludge," *J. Am. Water Works Assoc.* **10**, 2 (1923).
[14] *Am. J. Pub. Health*, **12**, 299 (1922).

the first to appear in noticeable numbers but that they gave way in time to other forms. The Peritrichs (Carchesium and Vorticella) appeared only after several days of aëration. The matured sludge seemed to be composed largely of zoogloeal masses with frequent colonies of Peritrichs and an occasional Hypotrichs (generally Euplotes).

Summary of Microscopic Observations May 3-17, 1921.

May 3		Plant started operation.
May 4	I.	A few Paramecium, paper fibers and miscellaneous vegetable cells.
May 5	I.	Paramecium, paper fibers and miscellaneous vegetable cells.
	II.	Gelatinous masses of fine bacterial filaments beginning to form.
May 6	I.	Large flocs of gelatinous masses of fine bacterial filaments.
	II.	Zoogloea, Paramecium, Colpidium.
May 7	I.	Branching gelatinous masses of fine bacterial filaments, Paramecium, Spyrogyra.
	II.	Paper fibers with much attached zoogloea. Many Paramecium, few Peritrichs (Vorticellidae), branched gelatinous masses of fine filaments.
May 8	I.	Branched gelatinous masses of fine filaments, Paramecium, Colpidium, 1 filament of Spyrogyra.
	II.	Branched gelatinous masses of fine bacterial filaments, few Holotrichs, mould hyphae and paper fibers.
May 9	I.	First appearance of Peritrichs in I. One filament of Spyrogyra, gelatinous masses of filamentous bacteria.
	II.	Increase in Peritrichs.
May 10	I.	Few ciliates, 80 percent of field consists of gelatinous masses.
	II.	Many Peritrichs.
May 11	I.	Largely gelatinous masses of filamentous bacteria; some Hypotrichs and Peritrichs.
	II.	Largely gelatinous masses of filamentous bacteria; fewer Peritrichs.
May 12		No change in character.
May 13		Increase in Peritrichs.
May 15, 16, 17		No changes in character.

In September the daily qualitative study of the sludge was resumed and a careful investigation of the forms in the zoogloeal masses undertaken. In November an interruption in the operation of the plant offered another opportunity to study the forms appearing during the building up of sludge. In this series of examinations which dates from November 17, quantitative estimations were made, using the Sedgwick-Rafter method of enumeration as Purdy did. Beginning with the 9th of December, $FeSO_4$, equivalent to 10 mg. per liter of Fe was added to the influent sewage for the purpose of determining its effect on the nitrogen cycle. It appeared to be without effect on the character of the organisms found. The results of these examinations are given in Table 47.

DISCUSSION OF DATA

In the study of the microbiology of activated sludge in its development from raw sewage there seems to be a definite succession or addition of forms, as the sludge develops. Beginning with the char-

TABLE 47.—*Organisms and Solids Found in Two-Tank Activated Sludge Unit.*[1]

Date	Minute ciliates and flagellates (thousands per cc.)	Peritrichida (thousands per cc.)	Holotrichida and heterotrichida (thousands per cc.)	Hypotrichida (thousands per cc.)	Larger flagellates (thousands per cc.)	Nematoda (thousands per cc.)	Beggiatoa filaments (thousands per cc.)	Standard units zoogloea masses (millions per cc.)	Total solids (milligrams per liter)	Percent solids vol. 1 hr. sed.
				Tank I						
Nov. 17	2,885.0	0.10	0.30	...	...	...	...	0.11	...	..
Nov. 18	215.0	0.30	1.40	...	...	...	0.20	0.38	2200	5
Nov. 19	90.0	0.60	1.90	...	...	...	0.30	0.37	2700	7
Nov. 20	...	...	...	...	...	...	...	...	...	7
Nov. 21	17.5	3.70	2.40	...	...	0.10	0.10	0.48	2930	8
Nov. 22	+	6.70	1.60	...	...	0.20	0.30	0.77	3370	9
Nov. 23	+	2.70	1.40	...	...	0.20	0.60	0.49	4030	11
Nov. 24	...	...	...	...	...	...	...	...	...	13
Nov. 25	+	8.60	3.60	1.20	...	0.10	0.30	1.08	4500	15
Nov. 26	+	14.07*	1.00	1.00	...	0.50	0.33	0.54	4900	18
Nov. 27	...	...	...	...	...	...	...	...	...	29
Nov. 28	+	6.50	3.00	3.80	...	0.70	0.40	0.10	5300	37
Nov. 29	+	12.85*	6.40	1.80	...	1.00	0.80	1.54	5800	48
Nov. 30	+	8.00	6.40	2.40	...	1.60	0.40	1.81	5430	68
Dec. 1	+	17.10	5.70	3.30	...	1.80	0.60	2.06	6140	76
Dec. 2	+	1.44	5.40	3.60	...	2.40	0.90	2.50	7350	78
Dec. 3	+	14.70	5.40	4.50	...	2.40	1.50	2.56	6480	84
Dec. 4	...	...	...	...	...	...	...	...	...	82
Dec. 5	+	4.00	0.60	0.80	...	1.00	0.40	1.11	6050	78
Dec. 6	...	3.00	4.80	2.70	...	3.30	1.20	1.70	...	..
Dec. 7	...	5.00	2.00	2.50	...	1.50	2.00	1.51	5300	75
Dec. 8	...	6.50	2.00	2.00	5.00	1.50	1.00	2.40	4800	74
Dec. 9	...	4.00	2.50	1.00	55.00	1.50	4.00	1.71	4410	74
Dec. 10	...	6.80	1.60	1.60	...	2.00	1.20	1.24	4100	52
Dec. 11	...	...	...	...	...	...	...	...	...	64
Dec. 12	+	7.60	1.20	3.20	4.20	4.00	2.80	2.10	4270	56
Dec. 13	...	12.90	2.20	4.00	...	...	4.50	1.84	4260	57
Dec. 14	...	15.00*	...	2.00	10.00	1.00	3.00	1.56	3770	57
Dec. 15	+	13.00	...	3.00	...	0.50	5.00	1.99	4010	59
Dec. 16	+	5.00	1.00	0.50	5.00	1.00	5.50	1.55	3120	58
Dec. 17	+	1.60	...	...	...	...	0.80	0.82	3060	55
Dec. 18	—	...	...	...	...	...	...	...	...	60
Dec. 19	+	6.00	...	1.60	...	0.80	3.20	1.41	3180	54
Dec. 20	+	5.20	0.40	1.60	...	...	4.40	1.32	2910	56
Dec. 21	+	4.80	...	0.40	...	...	1.20	0.82	2660	62
Dec. 22	+	5.10	...	0.60	...	...	3.00	0.79	2450	54
Dec. 23	+	2.40	0.40	0.40	...	...	1.60	0.51	2640	54
Dec. 24	+	5.00	0.40	2.60	...	...	0.80	0.71	2800	67
Dec. 25	...	...	...	...	...	...	...	...	...	63
Dec. 26	+	17.00*	0.50	1.50	...	...	0.50	2.39	3650	70
Dec. 27	+	10.80	1.00	2.60	...	0.20	0.80	0.89	3820	61
Dec. 28	+	12.40*	0.60	1.80	...	0.40	0.40	1.10	...	81

[1] Buswell and Long, *J. Am. Water Works Assoc.* **10**, 2 (1923).

* Colony or cluster of peritrichs present.

† The standard unit is used here as a measure of surface and equals 0.0004 sq. mm.

TABLE 47.—(*Contd.*)

Date	Minute ciliates and flagellates (thousands per cc.)	Peritrichida (thousands per cc.)	Holotrichida and heterotrichida (thousands per cc.)	Hypotrichida (thousands per cc.)	Larger flagellates (thousands per cc.)	Nematoda (thousands per cc.)	Beggiatoa filaments (thousands per cc.)	Standard units zoogloea masses (millions per cc.)	Total solids (milligrams per liter)	Percent solids vol. 1 hr. sed.
Tank II										
Nov. 17	...	...	...	...	...	...	...	...	...	..
Nov. 18	120.0	...	0.30	...	...	0.10	...	0.043	1370	1
Nov. 19	63.0	0.60	0.50	...	...	...	0.50	0.098	2360	2
Nov. 20	...	...	...	...	...	...	...	...	...	2
Nov. 21	75.0	1.50	0.70	...	...	...	0.20	0.224	1390	2
Nov. 22	12.5	2.90	0.80	0.10	...	...	0.30	0.132	1410	3
Nov. 23	+	1.10	0.40	...	...	...	0.20	0.231	1370	2
Nov. 24	...	...	...	...	...	...	...	...	...	3
Nov. 25	+	0.10	1.10	...	...	0.30	0.40	0.205	1120	2
Nov. 26	...	0.90	0.80	0.20	...	0.10	0.20	0.185	1220	2
Nov. 27	...	...	...	...	...	...	...	...	...	2
Nov. 28	+	1.20	0.50	0.20	...	0.10	0.10	0.145	1050	2
Nov. 29	+	0.50	1.00	...	...	0.10	0.10	0.055	900	1
Nov. 30	+	0.50	0.30	0.10	...	0.10	0.30	0.119	870	0
Dec. 1	+	0.60	0.10	...	...	...	...	0.024	890	..
Dec. 2	+	0.10	0.40	...	...	0.10	...	0.026	780	..
Dec. 3	...	...	...	...	...	...	...	...	790	..
Dec. 4	...	...	...	...	...	...	...	...	...	..
Dec. 5	...	...	...	...	...	...	...	...	1160	4
Dec. 6	...	5.10	0.60	0.90	...	0.90	...	0.725	...	27
Dec. 7	...	8.00	0.40	2.40	...	1.20	0.40	1.270	3970	60
Dec. 8	...	3.80	0.70	1.30	...	0.40	0.10	1.912	4570	64
Dec. 9	...	4.10	0.70	0.40	...	0.90	0.20	0.540	4610	62
Dec. 10	+	2.80	0.30	0.70	...	0.40	0.50	0.312	4780	74
Dec. 11	...	...	...	...	...	...	...	...	...	60
Dec. 12	+	13.20	0.40	2.40	...	2.40	2.40	2.010	4460	70
Dec. 13	+	16.00	7.50	5.50	...	3.00	2.50	3.400	4360	75
Dec. 14	+	16.50	0.50	2.50	...	2.50	3.50	2.012	4550	75
Dec. 15	+	9.50	0.50	5.00	...	2.50	1.50	1.987	3990	69
Dec. 16	+	9.00	...	...	...	1.50	3.00	1.712	4030	75
Dec. 17	+	7.60	0.40	0.40	...	0.80	1.60	1.500	3456	82
Dec. 18	...	...	...	...	...	...	...	...	...	82
Dec. 19	+	6.00	0.80	5.60	...	0.40	1.20	1.170	3610	86
Dec. 20	+	12.40	0.40	2.00	...	...	4 40	2.530	3610	88
Dec. 21	+	12.40	...	3.60	...	0.40	2.80	2.340	3530	92
Dec. 22	+	15.00	0.90	1.20	...	0.90	3.90	1.192	3270	83
Dec. 23	+	10.40	...	0.80	...	...	2.60	0.840	3000	92
Dec. 24	+	4.80	...	0.40	...	...	2.00	0.675	2690	89
Dec. 25	...	...	...	...	...	...	...	...	...	99
Dec. 26	+	3.80	2.20	2.00	...	0.20	0.20	1.025	3570	90
Dec. 27	+	4.80	1.80	2.40	...	...	0.20	1.170	3570	88
Dec. 28	+	6.40	0.80	0.80	...	...	0.20	1.405	...	87

[1] Buswell and Long, *J. Am. Water Works Assoc.* **10**, 2 (1923).

* Colony or cluster of peritrichs present.

† The standard unit is used here as a measure of surface only and equals 0.0004 sq. mm.

acteristic microörganisms of raw sewage as it is taken into the aëration chamber, there is a predominance of the minute flagellates and ciliates, with occasional Peritrichs and Holotrichs. In a few days the minute forms diminish in number until they become a negligible quantity while Peritrichs, Holotrichs, and Heterotrichs increase in number, the Peritrichs predominating throughout. As the minute forms become insignificant the gelatinous masses of the Chlamydobacteriacae and Nematodes appear, to be followed in a few days by the sudden appearance of Peritrichs. This point then brings us to the characteristic fauna and flora of the matured activated sludge, under the particular conditions of operation employed. Observations on the occurrence of the various groups of organisms have been summarized as follows:

Minute Ciliates and Flagellates.

The fauna of the samples taken November 17, two days after the beginning with raw sewage, was characteristic of the crude sewage. The minute ciliates and flagellates constituted practically the entire animal life. These forms continued to predominate in decreasing numbers until the 7th to 8th days, when, with the gradual formation of the sludge there was a marked decrease, with a predominance of larger forms. From November 22 on, through the period of observation, minute forms were present, but not in sufficient abundance to enumerate. Perhaps there were more of such forms present throughout the period, but were hidden from observation by the heavy sludge. Of the typical forms present, the minute free-swimming individuals predominated, while the spherical "rolling" colonies of Synura were abundant.

INFUSORIA.

Peritrichida.

As indicated in the table the Peritrichs were the most abundant forms throughout the entire period of observation. Beginning with a very low count they reached the point of predominance in eight days, with a count of 14,000 in eleven days, and continued to be the predominating type.

In many cases the extremely high count was due to colonial forms being present or to clusters of individuals not colonial.

From December 5 to 16, the Peritrichs were more or less quiescent or encysted. From the 5th to 10th only a very few individuals showed signs of activity; other individuals were largely either quiescent or encysted. From the 12th to 16th quiescent and active individuals were in about equal prominence.

The predominating type of Peritrichs was Vorticella. Individuals of the Pyxidium type were quite common on November 29, December 5, 8, and 13, and occasional individuals were recorded at other times.

Occasional colonies of Carchesium were observed. While not observed at any time in the unstained sludge, a stalk of Zoethamnium, with its characteristic continuous muscle, was found on a prepared slide stained with fuchsin.

Colonies and individuals were invariably attached, by means of the more or less long stalk to the amorphous particles of the sludge. The occasional free-swimming stalkless individuals resulting from division were observed.

Hypotrichida.

After ten days of operation Hypotrichs of the Euplotes type suddenly became abundant. No Hypotrichs had been observed up to November 23. The 24th being Sunday no observation was made. On the 25th the calculated count was 1200 per cubic centimeter. The count remained in the thousands the remainder of the period, reaching the highest count of 4500 on December 3 and next highest on the 31st.

In habits the characteristic Euplotes type was generally associated with the zoogleal masses of sludge where it apparently found its best forage.

The Holotrichida and Heterotrichida.

Organisms of these classes, principally Frontonia, were observed in the first sample taken, but in very limited numbers. With the evolution of the sludge they increased to a count of 6400 after fifteen days but showed a marked decrease from this point on, with a total absence in many observations.

There is a similar curve in the unit mass content of the sludge but the drop is not as sharp as in the case of the Holo- and Heterotrichous forms.

Suctoria.

Suctoria of two types were observed. Individuals of the type Genus Podophyra occurred very rarely, while individuals of the type, Genus Acineta were quite common. One or two were observed in the field on the following days, November 20, 21, 23, 24, 25 and December 1, 3, 5, 6, 19, 21 and 28.

THE WHEEL ANIMALCULES.

Rotatoria.

The rotifers were so rarely observed during the forty-six days that they hardly deserve mention. Because of the concentration of the sludge from the beginning of formation to the climax apparently the conditions were not suitable for the life and multiplication of the rotifers. However, in the small scale experiment carried on in laboratory and at the plant with large amounts of air, rotifers

became more abundant as the sludge became heavier and more concentrated.

In the small scale sludge experiment a much heavier sludge developed because only the effluent was removed. This condition seemed to be favorable to the rotifers.

Individuals of the type, Genus Brachionus, were observed but the forms most common were representative of the Genus Notommata.

ROUND WORMS.

Nematoda.

The Nematodes were of common occurrence in the experimental sludge after eleven days of operation. In the observations made on the large plant Nematodes were observed on the fourth day and gradually increased to 2400 per cc. on the 18th day, to a maximum of 3300 on the 21st day and then a gradual decrease that was comparable to the decrease in the rotifers.

ZOOGLŒAL MASSES.

Having briefly reviewed the fauna of the sludge, we should turn our attention to the sludge proper. On November 17, after two days, operation with raw sewage, units of zoogloeal mass numbered 115,000 (see table); by November 25, 1,089,500; by December 1st, 2,062,500. The count continued ranging between one and two million units throughout the period, a count typical of a climax sludge maintained at the given dilution.

The animal inclusions of the sludge made up a very small part of the entire mass. The base of the sludge was composed of zoogloeal masses intermixed largely with filamentous bacteria and occasional Zooglea ramigera.

It appears that the filamentous forms overwhelmingly predominate the sludge. The literature on filamentous forms is scattered and rather uncertain taxonomically. Therefore a more extended study of these inclusions and the literature is being made which will determine the species of the forms present. Crenothrix polyspora, Sphaerotilus dichotomus and Zoogloea ramigera were undoubtedly present, however, in large numbers.

BACTERIAL SURFACE.

Hering [15] long ago pointed out the importance of bacterial surface in sewage purification, though few definite data have been developed since his paper on the subject. From the table we may obtain a notion of the order of magnitude at least of the sludge surface in the activated sludge process. Take a case where two million standard units of zoogloeal masses were found per cubic centimeter in the

[15] *Eng. News*, **61**, 494.

aëration chamber. Each floc must have a lower surface equal at least to the upper surface so that leaving out the side surfaces we would have four million standard units of 0.0004 sq. mm. each or 16 sq. cm. of surface per cubic centimeter of volume. This figure does not include the surface of the protozoa or the free-swimming bacteria. If increased by fifty or one hundred percent it would probably approach more closely the correct value. This would mean a surface of approximately 500 sq. ft. of sludge surface in 1 cu. ft. of the aëration chamber.

SUMMARY.

In view of previous work of other authors cited and the data of the present paper we wish to propose the following statement of the theory of the activated sludge process. Activated sludge flocs are composed of a *synthetic* gelatinous matrix similar to that of Nostoc, or Merismopedia, in which filamentous and unicellular bacteria are imbedded and on which various protozoa and some metazoa crawl and feed. The purification is accomplished by ingestion and assimilation by organisms of the organic matter in the sewage and its resynthesis into the living material of the flocs. This process changes organic matter from colloidal and dissolved states of dispersion to a state in which it will settle out.

A calculation from data given indicates approximately 500 sq. ft. of sludge surface per cubic foot of aëration tank volume.

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